

GENERALIZED PHASE FIELD MODELS WITH MICROSCOPIC POTENTIALS

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In this thesis we study the solidification process of systems with intrinsic anisotropy. We aim at finding a bridge between the microscopic mechanisms and macroscopic description. This is achieved by generalizing the current phase field models in a way to incorporate microscopic physics and using asymptotic techniques to obtain macroscopic results. Upon analysis, expressions for physically relevant quantities are obtained. Also it is found that classical interface relations for both stationary and moving interfaces hold. These conditions are presented in various representations. Exemplary numerical calculations are carried out to illustrate the potential of the method as an additional tool in the study of interfaces. Furthermore, a concrete physical system with realistic parameters is considered to show how one can use the ideas developed here in order to get results that are of interest to other scientific communities, e.g. materials scientists and physicists.

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1.0 INTRODUCTION

1.1 SHARP INTERFACE MODEL OF SURFACES

The behavior of phase boundaries has been a developing subject of interest and an active research field in physics and mathematics for almost two centuries. One reason behind this is that phase boundaries naturally arise in many physical processes due to immiscibility of two or more substances with different physical properties. Hence, various phenomena such as capillarity effect, growth of grain boundaries, physics of binary alloys, formation of snow flakes fall under the category of interface science.

One of the oldest problems in the area dates back to Lamé and Clapeyron [1] who studied the freezing of ground. Their goal was to determine the thickness of solid crust generated by the cooling of a liquid at constant temperature filling the half space. In 1889, Stefan, while working on the freezing of the ground developed these ideas further and formulated the two phase model which came to be known as the Stefan Problem [2]. Mathematically, the problem was to determine both the temperature and interface, i.e., $(T(x, t), \Gamma(t))$, for $x \in \Omega \subset \mathbb{R}^d$ and $t \in \mathbb{R}^+$, satisfying the system of equations

$$\rho c T_t = K \Delta T \quad \text{in } \Omega \setminus \Gamma(t) \quad (1.1)$$

$$\rho l v = K \hat{n} \cdot [\vec{\nabla} T]_+^- \quad \text{on } \Gamma(t) \quad (1.2)$$

$$T - T_E = 0 \quad \text{on } \Gamma(t) \quad (1.3)$$

where v is the (normal) velocity of the interface, $[\vec{\nabla} T]_+^-$ is the difference in the gradient of the temperature between solid and liquid, K is the conductivity, ρ is the density, c is the

specific heat per unit mass, T_E is the equilibrium melting temperature, and l is the latent heat. The first of the above equations is the heat conduction equation in the bulk sides. The second one is known as the Stefan condition which is obtained by energy balance at the interface. The third equation reflects that the Stefan model designates a dual role for the temperature since the phase is determined by the sign of $T - T_E$.

The proof of existence and uniqueness of a solution to the Stefan problem was done in many stages. Proving the general existence of the solutions turned out to be a difficult problem for $d \geq 2$ (see e.g. [3]) that was finally solved by Meirmanov [4].

Parallel to the mathematical development was the progress in thermodynamics of surfaces. A physical quantity, known as the surface tension or the interfacial free energy density proved to be fundamentally important in understanding the behavior of interfaces. In simple terms it can be viewed as the "force per unit length" on the interface tending to oppose formation of "new" surface. It originates from unbalanced pull of the surface molecules. Another equivalent way to think of surface tension is to consider it as the excess free energy on the surface which arises due to the defect structure of interface.

Laplace, using mechanical arguments [83], had shown that the pressure difference between two sides of a liquid bubble is related to curvature of the surface. Likewise, Gibbs' work on liquids [5] suggested that the temperature at a curved interface in equilibrium should differ from T_E by a term proportional to the sum of principal curvatures, κ , and the surface tension, σ . Furthermore, heuristic arguments suggested that, for moving interfaces, an additional term proportional to the velocity of the interface should be present, leading to an interface condition known as the Gibbs-Thomson relation [7]:

$$T - T_E = -\frac{\sigma}{[s]_E} \kappa - \beta v \quad \text{on } \Gamma(t) \quad (1.4)$$

where $[s]_E$ is the entropy difference between the phases and β is a constant depending on the material.

Mathematically, the study of the system [(1.1), (1.2), (1.4)] is different from the classical Stefan problem in a fundamental way: the sign of the temperature no longer determines the phase of the material. Hence, the interface needs to be tracked in some way to determine the phase of each point. Existence theorems also posed significant problems and were proven

by various authors under some constraints [7], [8], [9]. Related problems of motion by mean curvature were studied in [10], [11], [12], [13].

The Stefan model, described by systems of equations (1.1)-(1.3), a priori assumes a zero thickness of the interface. Another way to handle the same problem can be done by combining the heat balance equation at the boundary and the heat diffusion equation in the bulk sides into one equation. In order to do that, one is required to introduce a new variable that will measure the "amount of phase" across the interface. This idea is related to Oleinik [14] who obtained the equation

$$\rho c T_t + \frac{l}{2} \varphi_t = K \Delta T \quad (1.5)$$

where φ is a Heaviside function. With the introduction of the curvature and/or velocity terms in (1.4) and the consequent inability of temperature to perform its dual role, arises the question of whether one can define a genuine variable ϕ , representing the phase, to replace the mathematical construct used in (1.1-1.3)

1.2 MEAN FIELD THEORY AND ORDER PARAMETER

While the above developments were taking place in mathematical analysis, novel ideas in physics were also advancing on ways to understand the phases of matter. The theory of phase transformations in statistical physics, which developed considerably during the twentieth century, provided some basic concepts. A representative (model) problem of such transition phenomena was ferromagnetism in which spins of atoms at the microscopic level presented a collective (ordered) behavior below a critical temperature.

Mean field theory, introduced by Weiss (see [84]), was one of the first attempts to explain ferromagnetism. It relied on the idea of an average, or effective, field M to account for the influence on one "spin" or atom, due to all others. This provided a vast simplification of the basic problem that involved summing over all possible states to calculate the partition function. On the other hand, Landau, in early 1930s, noticed that similar behavior arises in many types of phase transitions. He generalized the ideas of Weiss [15] and applied his version of mean field theory to critical phenomena and calculated the exponents with which

key thermodynamic quantities diverged at the critical point (e.g., the temperature at which the distinction between liquid and gas disappears). The motivation for this approach was the surprising similarity (which he called "universality") among the phenomena that are governed by seemingly unrelated mechanisms. The ingenious idea was that the free energy near the "critical point" could be expanded as an analytic function of the order parameter and the order parameter could be expanded as a function of the intensive quantities of the system (temperature, pressure etc.).

$$\begin{aligned} F &= a_0 + a_1 M + a_2 M^2 + \dots \\ M &= b_0 + b_1(T - T_c) + b_2(T - T_c)^2 + \dots \end{aligned} \tag{1.6}$$

where M is the order parameter, T_c is the critical temperature and a_i , b_i are coefficients that depend on the properties of the specific system at hand. By further symmetry considerations he argued that many coefficients in the above equations must be zero. This approach resulted in yielding the same critical exponents (hence the same critical behavior) for many physical systems which are seemingly different.

In the original theory the order parameter was a function of temperature but constant in space. Later, Landau and Ginzburg refined the theory by allowing the order parameter to be a function of a space variable. In order to account for the fluctuations they also assumed that the free energy depended on the gradient of the order parameter. Therefore, to the first degree of approximation, the free energy was given as a functional of M which had the form

$$\mathcal{F} = \int (c(\nabla M)^2 + a_2 M^2 + a_4 M^4 \dots) dx$$

In the early versions of mean field theory there were no correlations between the molecular fields. In other words the correlation function which is defined as

$$g(x, x') := \frac{(\langle M(x)M(x') \rangle_{avg} - \langle M(x) \rangle_{avg}^2)}{\langle M(x) \rangle_{avg}^2} \tag{1.7}$$

was equal to zero. But, in the extended formulation, since the order parameter has a dependence on the space variable, the correlation function is generally non-zero.

A natural question at this point is whether or not one should add higher gradient terms to the free energy. In essence, the treatment by allowing only the gradient square term can

be regarded as a truncation of the higher order modes in Fourier space. The justification for this approximation was that the correlation length (the distance scale for which spins or molecules feel the effects of one another) are very large and, in fact, diverge at the critical temperature.

Mean field theory in critical phenomena had some success as it led to convenient calculations of exponents that were at the right order of magnitude, but failed to provide the correct numerical values. The possibility of using mean field theories and "order parameters" in dynamical settings in critical phenomena was reviewed in [16]. Previously, Cahn and Hilliard had used a related diffuse interface approach in their study of surface tension [17]. Some related qualitative ideas also appeared in [18], [19].

1.3 DIFFUSE INTERFACE APPROACH TO STEFAN PROBLEM AND PHASE FIELD

The mean field or "order" parameter in critical phenomena led to the question of whether such a concept could be useful in resolving dynamical questions in a setting far from the critical point, namely that of an ordinary phase transitions. While this posed an interesting question in the physics community, the potential appeared to be limited. How could a theory that had produced disappointing calculations of key exponents in the regime for which it was designed possibly produce better results in a very different regime? The justification for the mean field approximation involved the very large correlation length. For an ordinary phase transition (e.g., solid-liquid) the correlation length is on an atomic scale of Angstroms, placing it near the opposite extreme from critical phenomena.

Adding to the obstacles was the fact that the study of critical phenomena relied heavily on an additional concept. Universality stipulates that the critical exponents do not depend on the details of the system such as the precise type of interaction but only on the basic entities of the system like symmetry group of the spins, dimension of the space, etc. Thus, universality provided additional justification for an approximation that tends to eliminate effects that involve short distances.

Consequently, if such an approach was to be a foundation for the quantitative study of the dynamics of phase transitions it faced a set of challenges: the absence of a concept such as universality, the requirement of quantitatively correct calculations, and finally a rationale for eliminating higher order fluctuation terms based on the short, rather than very long, correlation lengths. The last issue was considered in one of the early papers on this subject [20]. It was suggested that the justification for neglecting these terms is due to the fact that the transition length in the order parameter, or phase field, is small compared to the macroscopic scales of interest. This issue was further pursued in [21], [22] which examined the consequences of retaining arbitrarily higher order terms, and will be discussed at length in this thesis.

The problem of obtaining a quantitatively accurate description of the dynamics of interfaces using a phase field model led to a series of papers starting with [23], later incorporated into [24]. In this approach, in addition to the modified heat equation, an extra equation for the phase function was obtained from the relation $\tau\phi_t = -\delta F/\delta\phi$, where τ is a relaxation time and F is a free energy density that consisted of a double well potential $w(\phi)$ and an undercooling term $G(\phi)$.

$$\alpha\varepsilon^2\phi_t = \varepsilon^2\Delta\phi + w'(\phi) + \varepsilon\sigma^{-1}G'(\phi)(T - T_M) \quad (1.8)$$

$$\rho c T_t + \frac{l}{2}\phi_t = K\Delta T. \quad (1.9)$$

Then the system [(1.8)-(1.9)] is to be solved for $(T(x, t), \phi(x, t))$ for $(x, t) \in \Omega \times [0, T]$. With this approach the interface is simply the set of points on which ϕ vanishes, i.e.,

$$\Gamma_\varepsilon(t) := \{x \in \Omega : \phi_\varepsilon(x, t) = 0\},$$

avoiding the need for explicit conditions on the interface and the theoretical or computational requirement of tracking the interface. In fact, the first derivation of the dynamical relation (1.4) was obtained using the phase field model [20], [25]. The form of the phase equation (1.6a), with G as defined above, has the feature that ϕ is exactly ± 1 in the bulk phases, but one pays the price of an additional nonlinearity in G . The use of a linear function for $G(\phi)$,

representing linear entropy change through the interface leads to a term $(constant)(T - T_M)$ instead of the nonlinear term in (1.6a) but no longer retaining $\phi = \pm 1$ in the pure phases.

The research of the 1980's focused in part on the question of scaling the phase field equations [(1.8)-(1.9)] so that (i) the macroscopic parameters were identified, (ii) the interface thickness, ε , was determined independently of the other material parameters of the system and (iii) the sharp interface problems such as [(1.1-1.3)] or the classical Stefan model arose as the distinguished limits of the phase field equations in the limit as ε approaches zero [25]. In other words, one can take the limit $\varepsilon \rightarrow 0$ while retaining the value of the crucial material parameters such as the surface tension, σ . We shall discuss the issue in more detail in the following chapters.

Proving existence of solutions to phase field models and performing numerical computations, are generally easier than their sharp interface counterparts since, for any $\varepsilon > 0$, one has a system of smooth parabolic equations. However, rigorous proofs of the asymptotic convergence turned out to be considerably more difficult [28], [29], [30], [31], [32]. In recent years a number of new mathematical techniques have been utilized to understand the nature of solutions to phase field equations. These include global existence methods for generalizations of phase field equations and global attractor methods [33], [34], [35], [36], [37], [38], [39], [40].

A recent development in the phase field modelling was attaining orders high accuracy by modifying the terms in the functional. It was shown that if the phase equations are scaled properly, the interfacial thickness, ε , can be varied without significant change in the motion of the interface. This was verified by numerical computations in a series of papers including [26]. The significance of this result is that the atomic scale of ε could be increased by orders of magnitude rendering possible realistic computations. More recent research [27] showed that one could define phase field models and prove convergence at the ε^2 level. More precisely, if we denote the interface of the corresponding sharp interface problem by $\Gamma(t)$, then there exists a positive constants C and ε_0 such that the distance

$$dist(\Gamma(t), \Gamma_\varepsilon(t)) \leq C\varepsilon^2 \quad \text{for } \varepsilon < \varepsilon_0.$$

1.4 ANISOTROPY AND INTERFACES

The preceding discussion has been mainly based on the assumption that the surface tension is a constant independent of orientation (i.e., isotropic). The term anisotropy for interfaces refers to growth that is directionally dependent and is related to macroscopic properties such as surface tension and mobility. For most materials with a crystal structure, the surface tension is known to be anisotropic. Unfortunately, its experimental measurement is difficult. Early measurements [41], [42], [43] were performed only on transparent materials. For example, the surface tension of succinonitrile (often used in dendritic growth experiments) has cubic anisotropy of 0.5 % (i.e., the maximum surface tension for any orientation is 0.5% higher than the average) while the figure for pivalic acid is 5% [41]. More recently, experimentalists managed to measure the surface tension and the anisotropy in the free energy for a number of materials [44], [45].

On the other side, micro-gravity experiments were carried out on pure crystal-melt interfaces to measure the effect of convection [42]. Also, optical measurements were conducted to quantify the directional dependence of surface tension [41]. These experiments were complemented by computational modelling using the phase field approach [67] and other methods [68].

The theoretical research in the 1990s was more towards obtaining macroscopic equations of evolution as probabilistic limits of discrete spin dynamics [71], [72]. [75], [72], [74]. Two dimensional proof of Wulff Construction (a scheme to draw equilibrium surfaces of solidifying materials) came about the same time [70]. Sharp interface limits of Cahn Hilliard Equations with non-local potentials and Stochastic Ising models were also studied [73].

During the past decade simulations also gained a boost in this subject. The research has evolved considerably along several avenues. One of them is the modern version of the so called cleaving method, originally introduced by Broughton and Gilmer [46]. Recently, this technique was refined and was used to determine both the value and anisotropy of surface tensions for various systems. Another method, which is known as the Fluctuation Method, is based on monitoring the interfacial fluctuations during molecular dynamic simulations [48]. In general, the first method gives better results for the absolute value of free energy [49],

while the second one captures the anisotropy better [50]. Both methods have advantages and disadvantages that complement each other [51], [52], [53]. Yet another kind of diffuse interface modelling is via using Willmore regularization [79]. The main idea of this approach is to introduce a curvature dependent extra term in the surface tension which is controlled by a variable (say β). The new term is designed to penalize the high curvatures at the corners (cusps) and the ill posedness due to high anisotropy. For the solutions, adaptive multi scale finite difference schemes can be employed to simulate the evolution [78], [77]. The equilibrium shapes that are obtained (by letting $\beta \rightarrow 0$) with this method are also in good agreement with the sharp interface results.

Derivation of macroscopic results concerning anisotropy however, are not as abundant. Following the works of Gibbs and Curie, Wulff [54] published a key result at the turn of the last century. This is essentially a prescription to draw equilibrium surfaces (with or without anisotropy). A half-century later Herring presented a derivation of an interface equilibrium relation [55] which relates the anisotropic surface tension and its derivatives to the temperature of the interface

$$[s]_E (T - T_E) = -\kappa \{ \sigma(\theta) + \sigma''(\theta) \} \quad (1.10)$$

where T is the temperature at the interface and T_E the equilibrium coexistence temperature, $[s]_E$ is the entropy difference between phases, θ is the angle between the normal of the interface and a fixed axis, and σ is the surface tension.

Around 1970s, Hoffman and Cahn introduced the capillarity vector or the ξ -vector [56], [57] which they defined by $\xi = \nabla(r\sigma(n))$ and neatly generalized Gibbs-Thomson-Herring's result to three dimensions as

$$-u[s]_E = \nabla \cdot \xi$$

They also showed that the surface tension could be regarded as the normal component of the capillarity vector on the interface. They constructed the ξ -plot which directly gave the equilibrium position of the interface through the relation

$$\xi = \frac{\Delta f}{3} x$$

where Δf is the free energy difference between phases per unit volume .

The treatment of anisotropic interfaces via the diffuse interface approach was attempted in different ways. Heuristic methods were developed to incorporate anisotropy into the phase field equations. This was initially done by directly putting the directional dependence into the parameters of the free-energy functional in a way that made them functions of the gradient of the phase field. By further generalization [58], a second method enables one to import the Hoffman-Cahn's ξ – *vector* into the phase field formulation by rewriting the interaction part of the Hamiltonian in terms of the ξ vector [59]. While these related methods enabled calculations and lead to correct macroscopic conditions [60], they were implicit, i.e., they did not provide a direct analytical way of calculating the anisotropy from the type of molecular interactions.

On the other hand density functional and explicit phase field methods provided more ways to quantify anisotropy. The first density functional calculation on the interfacial free energy and its orientation dependence was done by Haymet and Oxtoby [61], [62]. A similar treatment was followed by Shih et. al. [63], Curtin [64] and others [65], [66].

Anisotropy was included explicitly in the phase field theory in an early paper [20]. A two-fold anisotropy was assumed in the microscopic interactions which yielded the following interface condition in the asymptotic limit

$$(T - T_E) [s]_E = -\kappa \{ \sigma(\theta) + \sigma''(\theta) \} - \frac{\tau}{\xi_A^2} v \sigma(\theta) \quad (1.11)$$

$$\xi_A^2(\theta) := \xi^2 + (\xi_1^2 - \xi^2) \cos^2(\theta)$$

where ξ_1 is proportional to the surface tension in the 1–direction and ξ_2 in the 2–direction.

An important observation regarding this approach [21],[81] was that the interactions with higher anisotropy (four-fold, six-fold) does not survive the truncation of higher modes in the free energy which results in second order phase equation (1.6a). In Chapter 2 we shall explicitly see how higher fold anisotropic terms vanish in the process of averaging. So, in order to see the effect of anisotropy, one needs to retain higher order modes, and therefore, consider higher order differential equations analogous. For instance, for a six-fold anisotropic lattice one should extract the corresponding sixth order differential equation to capture the anisotropic effects, for in the lower orders the anisotropy will be "washed out".

Recently, approaches along similar lines appeared in the literature (see [76]) by the so called Extended Cahn-Hilliard Model. In this approach, The original Cahn-Hilliard energy function is expanded in Taylor series up to fourth or sixth order in the derivatives in a way that the crystal symmetry is preserved. Then, higher order Cahn-Hilliard equation is solved numerically for the evolution of the interface. Again, the anisotropy is hidden in the higher order derivative terms.

1.5 THE WULFF SHAPE

As noted above, the surface tension is one significant parameter that affects the equilibrium pictures of surfaces. When single particle is embedded into another phase of fixed volume its interface assumes the orientation that minimizes its total surface energy, i.e., $\int \gamma(\hat{n})dA$. Specifically, in solidification, the **Wulff shape** is the shape of a solid under the undercooling temperature $u \equiv -1$.

1.6 OUTLINE OF THE THESIS

In this thesis, we pursue the problem of anisotropy in two different ways. In the first approach a more general free energy functional is constructed by including the effects of higher order correlation terms that are usually ignored in standard phase field models. The second way on the other hand takes a more direct approach to the same problem. Instead of the usual form of the energy functional with derivatives, an integral form is formulated which is advantageous from analytical and computational perspective.

In the first approach one does not assume the standard functional form of the free energy but starts from the following form of the free energy

$$\mathcal{F}[\phi] = \mathcal{H}_I + \int_{\Omega} dx W(\phi, u) := \int_{\otimes} \frac{1}{4} J(x-y)(\phi(x) - \phi(y))^2 + \int_{\Omega} \frac{w(\phi)}{a} - G(\phi, u) \quad (1.12)$$

and tries to derive a more general expression that involves higher order derivatives of the phase field. In above $J(x)$ is the strength of the local interactions and ϕ is the phase field. $w(\phi)$ represents the contribution of the entropy to the free energy which is zero in the bulk sides (no accessible state). Its original singular form is often replaced by a smooth function with two minima whose magnitude can be tuned by the parameter "a", the well-depth. Finally, the $G(\phi, u)$ function is the phase field temperature coupling term.

After some manipulations the interaction Hamiltonian can be put in the more suitable form. For most realistic systems in two dimensions the anisotropic interactions are expected to take the form $J(r, \theta) = f(r) \sum_{n=0}^N [J_c(n) \cos 2n\theta + J_s(n) \sin 2n\theta]$. Then, the detailed analysis will show that for $2M^{th}$ fold anisotropy in the interactions (in two dimensions) one needs to retain $2M^{th}$ order phase field equation, i.e.,

$$\begin{aligned} \tau \phi_t = & - \int \sum_{m=1}^M \sum_{n=0}^m a c_{2m,n} S(m) (D_{11} + D_{22})^{m-n} [J_c(n) \Re(D_1 + iD_2)^{2n}] \phi \\ & + w'(\phi) - a G'(\phi) u \end{aligned} \quad (1.13)$$

where D_1, D_2 are derivatives with respect to coordinate variables, $c_{2m,n}$ is a combinatorial factor that comes from the angular part of integrations and $S(m)$ is a scaling factor that is related to radial integrals.

Assuming an asymptotic expansion for the phase field and the appropriate scaling for the coefficients in the equations, one can write down the field equation in the local coordinates (z, s) . Once this is done, (upon finding the stationary solutions) the surface tension, through a local interpretation of the free energy is obtained as

$$\sigma = \int_{-\infty}^{\infty} dz \sum_{m=1}^M f_0 (-1)^{m+1} m \left(\frac{\partial^m \Phi^0}{\partial z^m} \right)^2 \sum_{n=0}^m \tilde{c}_{2m,n} J_c(n) \cos 2n\theta$$

Furthermore, it can be shown that formal asymptotic solutions satisfy the Gibbs-Thomson-Herring condition at the interface, i.e.,

$$[s]_E (T - T_E) = -\kappa \{ \sigma(\theta) + \sigma_{\theta\theta}(\theta) \}$$

In the second part of the thesis we will approach the problem from a different perspective. We shall directly work with the integral form of the Hamiltonian thereby avoiding transforms

and approximations. The free energy in this approach is assumed to consist of both local and non local terms : ζ

$$\mathcal{F}[\phi] = \frac{\lambda}{2} \int a(\vec{\nabla} \phi(x)) dx + \frac{(1-\lambda)}{4} \int J_\varepsilon(x-y)(\phi(x) - \phi(y))^2 dx dy + \int_\Omega dx W(\phi, u) \quad (1.14)$$

where the first term represents the local type of interactions whose weight is determined by the parameter λ . ($0 \leq \lambda \leq 1$) and J_ε is defined as $J_\varepsilon(x) := J(x/\varepsilon)\varepsilon^{-n}$. Then, in this formulation, the phase field equation is actually an integro-differential equation, i.e.

$$\alpha \varepsilon^2 \phi_t = \varepsilon^2 \lambda A : D^2 \phi + (1-\lambda) J_\varepsilon * \phi - \phi - W'(\phi) + \varepsilon u G'(\phi) \quad (1.15)$$

There are several benefits of this approach both mathematically and practically which we shall discuss later in more detail. First and foremost It is much easier to establish the existence and uniqueness of the solutions using the existing theory [80].

Solving (1.15) in the special case of planar interface, the interfacial free energy density can be defined by

$$\sigma(\zeta) = \int_{\zeta \mathbb{R}} \left(\frac{\lambda \varepsilon}{2} \nabla \phi \otimes \nabla \phi + \frac{(1-\lambda)}{2} [\phi - J_\varepsilon * \phi] + \frac{W(\phi)}{\varepsilon} \right) H^1(dx) \big|_{\phi(x)=Q(\zeta, \frac{(x-x_0) \cdot \zeta}{\varepsilon})} \quad (1.16)$$

where $\phi(x) = Q(\zeta, \frac{(x-x_0) \cdot \zeta}{\varepsilon})$ is the stationary solution for a planar interface and $H^1(dx)$ is the length element of the line $\zeta \mathbb{R}$. The tensor product of two vectors b and c is denoted by $(b \otimes c)_{ij} = b_i c_j$. Then, the surface tension of the interface is just the value of σ for $\zeta = \hat{n}$.

After working out the asymptotic analysis which requires a fair amount of differential geometry the interface condition in arbitrary dimensions can be obtained (analogous to Gibbs-Thomson-Herring relation)

$$u + u + \alpha(\hat{n})v + \vec{\nabla} \hat{n} : D^2 \sigma(\hat{n}) = 0 \quad (1.17)$$

which can be equivalently stated in terms of principle curvature directions as

$$u + \alpha(\hat{n})v + \sum_{i=1}^{N-1} \kappa^i \sigma_{\tau_i \tau_i}(\hat{n}) = 0, \quad (1.18)$$

where $\kappa^1, \dots, \kappa^{N-1}$ be the principal curvatures and the $\tau_1, \dots, \tau_{N-1}$ the principal directions. The same result can also be given by level set representation

$$\nabla \hat{n} : D^2 \sigma(\hat{n}) = \operatorname{div} \left(\sigma_\zeta \left(\frac{\nabla \Psi}{|\nabla \Psi|} \right) \right). \quad (1.19)$$

where Ψ is a function (not necessarily having a physical origin like the phase field) and $\Gamma_t = \{x \mid \Psi(x, t) = 0\}$ is the level set.

2.0 HIGHER ORDER PHASE FIELD EQUATIONS

Our objective in this chapter is to derive a set of phase field equations that are of arbitrarily high order via anisotropic interactions at the microscopic level. From these equations we shall deduce the macroscopic conditions on the interface and the relevant physical quantities.

Consider a lattice gas type model in the continuum limit within a spatial domain Ω in d - dimensions. We define an order parameter (phase field) $\phi(x, t)$ and interaction parameter $J(x - x')$ which satisfies the symmetry relation

$$\int_{x \in \Omega} dx J(x) x_1^{j_1} \dots x_d^{j_d} = 0 \quad \text{if } j_i \text{ is odd for at least one } i \in (1, 2, \dots, d) \quad (2.1)$$

Each of the following three examples satisfies this symmetry condition.

Example 1. Any isotropic J (i.e., depending only on the magnitude of the argument).

Example 2. Any J of the form

$$J(r, \theta) = J_0(r) + \delta \sum_{n=1}^N f(r) \{J_c(n) \cos(2n\theta) + J_s(n) \sin(2n\theta)\}$$

where (r, θ) are polar coordinates for $d = 2$.

Example 3. Any J such that $J(x_1, \dots, x_i, \dots, x_d) = J(x_1, \dots, -x_i, \dots, x_d)$ for each $i \in \{1, 2, \dots, d\}$. ■

2.1 FORMAL (PHYSICAL) DERIVATION OF THE FREE ENERGY

Before obtaining the functional form of the free energy that we are going to analyze, we present a formal derivation of it to give a physical motivation of the problem. For this purpose we make certain assumptions on the way until we reach the desired form of the free energy. After that we will take this form as our free energy definition and continue from there.

In discrete lattice gas models (Ising type systems) the interaction energy is given by a sum over all the lattice points.

$$H_I = - \sum_{i,j \ (i \neq j)} J_{ij} S_i S_j \quad (2.2)$$

Here, J_{ij} is the strength of the local interaction energy between the i^{th} site and j^{th} site and S_i and S_j are the phase (or spin) variables at those lattice points analogous to ϕ for the continuum. For continuum models, phase variables depend on the position continuously and the discrete sums are replaced by integrals. So, analogously the full interaction Hamiltonian \mathcal{H}_{If} can be written as

$$\mathcal{H}_{If} = -\frac{1}{2} \int_{x,x' \in \Omega} dx dx' J(x-x') \phi(x) \phi(x'). \quad (2.3)$$

We also assume that J vanishes beyond a distance R_∞ although this assumption can be relaxed with conditions on the rate of decay.

The use of Fourier space facilitates the analysis. In order to use Fourier transforms, we need to extend Ω to all of \mathbb{R}^d . However, this introduces divergences in the double integral above since ϕ is constant in the pure (bulk) phases. This issue, which arises frequently in field theories can be resolved in several ways. One way is to define the Hamiltonian as

$$\mathcal{H}_{If} := \frac{1}{4} \int_{x,x' \in \Omega} dx dx' J(x-x') (\phi(x) - \phi(x'))^2 \quad (2.4)$$

and proceed. A second way is to change the bulk value convention from $\phi = \mp 1$ to $\phi = 1$ in the (finite size) solidifying crystal and $\phi = 0$ in the rest of the space (liquid bulk). Thus, we assume $\Omega := \mathbb{R}^d$ below and assume the form (2.4) for the Hamiltonian and use the

second convention to secure the mathematical validity of the formal manipulations. Then the Fourier transform of $J(x)$ can be written as

$$\widehat{J}(q) := \int_{x \in \mathbb{R}^d} e^{-iq \cdot x} J(x) dx \quad (2.5)$$

and similarly,

$$\widehat{\phi}(q, t) := \int_{x \in \mathbb{R}^d} e^{-iq \cdot x} \phi(x, t) dx. \quad (2.6)$$

We will drop the t dependence when it is not relevant. Writing $e^{-iq \cdot x}$ in a Taylor series,

$$e^{-iq \cdot x} = \sum_{n=0}^{\infty} \frac{(-iq \cdot x)^n}{n!} = \sum_{n=0}^{\infty} (-i)^n \frac{(q \cdot x)^n}{n!} \quad (2.7)$$

we substitute the expansion into the definition of $\widehat{J}(q)$ to obtain,

$$\widehat{J}(q) := \int_{x \in \mathbb{R}^d} \left\{ J(x) + \left(\sum_{n=1}^{\infty} (-i)^n \frac{(q \cdot x)^n}{n!} \right) J(x) \right\} dx \quad (2.8)$$

where the first term, which can also be expressed as $\widehat{J}(0)$, is the mean field contribution to interaction Hamiltonian. The other terms are the higher order correlation terms.

Let $\|J\|$ be defined by $\|J\| := \int_{x \in \mathbb{R}^d} J(x) dx$. Then,

$$\begin{aligned} \mathcal{H}_{If} &= \int_{x, x' \in \mathbb{R}^d} \frac{1}{2} J(x - x') \phi(x)^2 - \int_{x, x' \in \mathbb{R}^d} \frac{1}{2} J(x - x') \phi(x) \phi(x') \\ &= \int_{x, x' \in \mathbb{R}^d} \frac{1}{2} \|J\| \phi(x)^2 - \frac{1}{2} \int_{q \in \mathbb{R}^d} dq \widehat{J}(q) \widehat{\phi}(q) \widehat{\phi}(-q) \end{aligned} \quad (2.9)$$

Note that in the first line, by the choosing the convention for ϕ to be zero outside the finite size crystal (see the discussion after (2.4)), both integrals are converging. Now rewriting

$\widehat{J}(q) = \int_{x \in \mathbb{R}^d} e^{-iq \cdot x} J(x) dx$ we have

$$\begin{aligned} & -\frac{1}{2} \int_{x \in \mathbb{R}^d} dx \int_{q \in \mathbb{R}^d} dq \{ e^{-iq \cdot x} J(x) \} \widehat{\phi}(q) \widehat{\phi}(-q) \\ &= -\frac{1}{2} \int_{x \in \mathbb{R}^d} dx J(x) \int_{q \in \mathbb{R}^d} dq \{ e^{-iq \cdot x} \} \widehat{\phi}(q) \widehat{\phi}(-q) \\ &= -\frac{1}{2} \int_{x \in \mathbb{R}^d} dx J(x) \int_{q \in \mathbb{R}^d} dq \left\{ 1 + \sum_{n=1}^{\infty} \frac{(iq \cdot x)^n}{n!} \right\} \widehat{\phi}(q) \widehat{\phi}(-q) \end{aligned} \quad (2.10)$$

The second line was made possible by using a version of Fubini theorem since we have the inequality

$$\int_{q \in \mathbb{R}^d} dq \int_{x \in \mathbb{R}^d} dx \left| e^{-iq \cdot x} J(x) \widehat{\phi}(q) \widehat{\phi}(-q) \right| \leq \|J\| \int_{q \in \mathbb{R}^d} dq \left| \widehat{\phi}(q) \widehat{\phi}(-q) \right| < \infty.$$

The inequality is valid because $\phi(x)$ is assumed to be zero outside a finite region and it is in the Schwarz class, and smooth enough that $\widehat{\phi}$ decreases sufficiently rapidly at infinity for the integral to be finite.

We expand $(q \cdot x)^n = (q_1 x_1 + \dots + q_d x_d)^n$ in the third line of (2.10) and want to change the order of the summation and the integrals in order to take the summation outside. Let us investigate the first interchange, i.e.,

$$\int_{q \in \mathbb{R}^d} dq \left\{ \sum_{n=0}^{\infty} \frac{(iq \cdot x)^n}{n!} \right\} \widehat{\phi}(q) \widehat{\phi}(-q) \stackrel{?}{=} \sum_{n=0}^{\infty} \int_{q \in \mathbb{R}^d} dq \frac{(iq \cdot x)^n}{n!} \widehat{\phi}(q) \widehat{\phi}(-q).$$

Now, we try to estimate the series from above

$$\begin{aligned} \sum_{n=1}^{\infty} \left| \frac{(iq \cdot x)^n}{n!} \widehat{\phi}(q) \widehat{\phi}(-q) \right| &\leq |x|^n \sum_{n=1}^{\infty} \left| \frac{|q|^n}{n!} \widehat{\phi}(q) \widehat{\phi}(-q) \right| \\ &\leq |x|^n \sum_{n=1}^{\infty} \frac{M_n}{n!} \left| \widehat{\phi}(-q) \right| \end{aligned}$$

Each M_n is a number independent of q . We assume that it does not grow fast by increasing n . If we assume that the sum $\sum_{n=1}^{\infty} \frac{M_n}{n!}$ is finite, then the series converges uniformly by M-Test for fixed x . The second interchange, i.e.,

$$\int_{x \in \mathbb{R}^d} dx J(x) \sum_{n=0}^{\infty} \int_{q \in \mathbb{R}^d} dq \frac{(iq \cdot x)^n}{n!} \widehat{\phi}(q) \widehat{\phi}(-q) = \sum_{n=0}^{\infty} \int_{x \in \mathbb{R}^d} dx J(x) \int_{q \in \mathbb{R}^d} dq \frac{(iq \cdot x)^n}{n!} \widehat{\phi}(q) \widehat{\phi}(-q)$$

can also be made possible by another application of Fubini theorem under certain assumptions. We need to show $\int_{x \in \mathbb{R}^d} \sum_{n=0}^{\infty} |dx J(x) \int_{q \in \mathbb{R}^d} dq \frac{(q \cdot x)^n}{n!} \widehat{\phi}(q) \widehat{\phi}(-q)| < \infty$. This will follow from

$$\begin{aligned} \int_{x \in \mathbb{R}^d} \sum_{n=0}^{\infty} \left| dx J(x) \int_{q \in \mathbb{R}^d} dq \frac{(q \cdot x)^n}{n!} \widehat{\phi}(q) \widehat{\phi}(-q) \right| &< \int_{x \in \mathbb{R}^d} \sum_{n=0}^{\infty} dx J(x) \frac{|x|^n}{n!} \int_{q \in \mathbb{R}^d} dq |q|^n \widehat{\phi}(q) \widehat{\phi}(-q) \\ &< \int_{x \in \mathbb{R}^d} \sum_{n=0}^{\infty} dx J(x) \frac{|x|^n}{n!} M_n K < \infty \end{aligned}$$

provided that M_n does not grow very fast with increasing n . For instance, if $M_n \sim \alpha^n$ for some $\alpha > 1$, then, for sufficiently rapidly decaying J , we have

$$\int_{x \in \mathbb{R}^d} \sum_{n=0}^{\infty} dx J(x) \frac{|x|^n}{n!} M_n K < \int_{x \in \mathbb{R}^d} dx J(x) e^{\alpha x} K < \infty$$

Having shown the validity of the interchange under these assumptions, we now use the notation $\sum_{j_1+\dots+j_d=n}$ below to denote the sum over all nonnegative integers j_1 through j_d such that $j_1 + j_2 + \dots + j_d = n$. Also, we truncate the summations at a finite order and take what remains (the approximation of the full Hamiltonian) as our interaction term. This means some loss of physics. Nevertheless it will be a better approximation than the older phase field models in which the truncation was made at the second order.

Let us denote by $\mathcal{H}_I(M)$ the **approximate** Hamiltonian which is obtained by truncating the infinite series at a finite M , where M is a positive even integer with $M > 2$. Then we have the expression

$$\begin{aligned} \mathcal{H}_I(M) &= -\frac{1}{2} \sum_{n=1}^M \sum_{j_1+\dots+j_d=n} \int_{x \in \mathbb{R}^d} \int_{q \in \mathbb{R}^d} dx dq \frac{(-i)^n}{j_1! \dots j_n!} (q_1 x_1)^{j_1} \dots (q_d x_d)^{j_d} J(x) \widehat{\phi}(q) \widehat{\phi}(-q) \quad (2.11) \\ &= -\frac{1}{2} \sum_{n=1}^M \sum_{j_1+\dots+j_d=n} \int_{q \in \mathbb{R}^d} dq \frac{(-i)^n}{j_1! \dots j_n!} q_1^{j_1} q_2^{j_2} \dots q_d^{j_d} \widehat{\phi}(q) \widehat{\phi}(-q) \int_{x \in \mathbb{R}^d} dx J(x) x_1^{j_1} \dots x_d^{j_d}. \end{aligned}$$

Notice that with the symmetry assumption (2.1), for which the isotropic interaction is a special case, terms of odd j_i will vanish in the last integral above. We can then set $j_i = 2k_i$, $n = 2m$ and simplify the q factors as follows:

$$\begin{aligned} &\int_{q \in \mathbb{R}^d} q_1^{2k_1} q_2^{2k_2} \dots q_d^{2k_d} \widehat{\phi}(q) \widehat{\phi}(-q) dq \quad (2.12) \\ &= \int_{q \in \mathbb{R}^d} dq q_1^{2k_1} q_2^{2k_2} \dots q_d^{2k_d} \int_{y \in \mathbb{R}^d} dy \phi(y) e^{-iq \cdot y} \int_{y' \in \mathbb{R}^d} dy' e^{iq \cdot y'} \phi(y') dy' \\ &= \int_{q \in \mathbb{R}^d} \int_{y \in \mathbb{R}^d} dq dy q_1^{k_1} q_2^{k_2} \dots q_d^{k_d} e^{-iq \cdot y} \phi(y) \int_{y' \in \mathbb{R}^d} dy' q_1^{k_1} q_2^{k_2} \dots q_d^{k_d} e^{iq \cdot y'} \phi(y') \\ &= \int_{q \in \mathbb{R}^d} \int_{y \in \mathbb{R}^d} dq dy (D_1^{k_1} D_2^{k_2} \dots D_d^{k_d} e^{-iq \cdot y}) \phi(y) \int_{y' \in \mathbb{R}^d} dy' (D_1^{k_1'} D_2^{k_2'} \dots D_d^{k_d'} e^{iq \cdot y'}) \phi(y'). \end{aligned}$$

The prime above $D_1^{k_1'}$ serves only as a reminder that, in the second integral we are integrating over y' . We can now shift the derivative terms onto ϕ by integration by parts. Note that

the derivatives of ϕ vanish at infinity, since this corresponds to a pure phase of the material. Hence, we have

$$\int_{q \in \mathbb{R}^d} dq q_1^{2k_1} q_2^{2k_2} \dots q_d^{2k_d} \widehat{\phi}(q) \widehat{\phi}(-q) \quad (2.13)$$

$$\begin{aligned} &= \int_{q \in \mathbb{R}^d} dq \int_{y \in \mathbb{R}^d} dy (D_1^{k_1} D_2^{k_2} \dots D_d^{k_d} e^{-iq \cdot y}) \phi(y) \int_{y' \in \mathbb{R}^d} dy' (D_1^{k_1'} D_2^{k_2'} \dots D_d^{k_d'} e^{iq \cdot y'}) \phi(y') \\ &= \int_{y' \in \mathbb{R}^d} dy' \int_{y \in \mathbb{R}^d} dy \int_{q \in \mathbb{R}^d} e^{iq \cdot y'} e^{-iq \cdot y} dq [D_1^{k_1} D_2^{k_2} \dots D_d^{k_d} \phi(y)] [D_1^{k_1'} D_2^{k_2'} \dots D_d^{k_d'} \phi(y')] \\ &= \int_{y \in \mathbb{R}^d} dy [D_1^{k_1} D_2^{k_2} \dots D_d^{k_d} \phi(y)]^2. \end{aligned} \quad (2.14)$$

Using these, the (approximate) interaction Hamiltonian can be written as

$$\mathcal{H}_I(M) = \frac{1}{2} \sum_{m=1}^M \sum_{k_1 + \dots + k_d = m} (-1)^{m+1} \int_{y \in \mathbb{R}^d} \frac{[D_1^{k_1} D_2^{k_2} \dots D_d^{k_d} \phi(y)]^2}{(2k_1)! \dots (2k_d)!} \int_{x \in \mathbb{R}^d} x_1^{2k_1} \dots x_d^{2k_d} J(x). \quad (2.15)$$

This was obtained in [21] and it generalizes the $\int (\nabla \phi)^2$ term of the original (second order) phase field equations. For subsequent calculations, it will be convenient to rewrite this in a form that facilitates combinatorial analysis. Integrating by parts over dy_i , k_i times for all $i \leq d$ we have

$$\mathcal{H}_I(M) = -\frac{1}{2} \sum_{m=1}^M \sum_{k_1 + \dots + k_d = m} \int_{y \in \Omega} \frac{[D_1^{k_1} D_2^{k_2} \dots D_d^{k_d} \phi(y)] \phi(y)}{(2k_1)! \dots (2k_d)!} \int_{x \in \mathbb{R}^d} x_1^{2k_1} \dots x_d^{2k_d} J(x). \quad (2.16)$$

The Helmholtz free energy is defined as the difference between the internal energy and the “entropic energy” $\mathcal{F} = E - TS$. Since we assume that there are only two phases, the entropic part of the free energy can be represented as a double-well potential with minima at or near $\phi = 1, -1$ and we can write the (approximate) free energy in terms of ϕ and the reduced temperature $u := T - T_E$

$$\mathcal{F}_M[\phi] = \mathcal{H}_I(M) + \int_{\mathbb{R}^d} dx W(\phi, u) =: \mathcal{F}_W[\phi, u] \quad (2.17)$$

where the function $W(\phi, u)$ consists of two parts:

$$W(\phi, u) = \frac{w(\phi)}{a} - G(\phi, u)$$

with $w(\phi)$ as the double-well potential and $G(\phi, u)$ the temperature-phase field coupling. Here, a and ε are parameters that measure the well-depth and interface thickness, respectively. We can define the free energy density, F , by $\mathcal{F} = \int_{\Omega} F$. In the earliest phase field papers, these functions were chosen to be of the form

$$\mathcal{F}_W[\phi, u] := \int_{\mathbb{R}^d} dx \left[\frac{(\phi^2 - 1)^2}{8a} - Bu\phi \right]$$

where B is a constant that is related to the material parameters, $B := \frac{[s]_E}{(\Phi_+ - \Phi_-)}$, and Φ_{\pm} are the roots of $W(\phi, u)$. With this choice of G one has the simplest coupling. It is also possible to use a broader range of functions for G (as discussed later) that will lead to the same macroscopic equations.

2.2 MACROSCOPIC RELATIONS IN THE ISOTROPIC CASE

In this section we derive our results for isotropic materials. Part of these results were presented with a different approach in an earlier paper [22].

Note: In the sequel the **approximate** Hamiltonian that was derived in the previous section on physical grounds will be taken as the interaction Hamiltonian of our model. So, for the rest of this chapter the words Hamiltonian and free energy refer to the functionals (2.19) and (2.24).

For clarity, we will state and derive our results in $2 - d$, but an n dimensional version of the main results is included in the Appendix. The first step is to evaluate the integral $\int_{x \in \Omega} dx x_1^{2k_1} x_d^{2k_2} J(x)$ in the Hamiltonian for $J(x) = J(|x|)$. We do this in polar coordinates and use some combinatorial identities. We define,

$$\begin{aligned} A(m; k_1, k_2) &:= \frac{1}{(2k_1)!(2k_2)!} \int_0^{2\pi} \int_0^{R_{\infty}} J(r) r dr (r \cos \theta)^{2k_1} (r \sin \theta)^{2k_2} d\theta = \\ &= \int_0^R J(r) r^{1+2m} dr \frac{1}{(2k_1)!(2k_2)!} \int_0^{2\pi} (\cos \theta)^{2k_1} (\sin \theta)^{2k_2} d\theta \end{aligned} \quad (2.18)$$

where $S(m) := \int_0^{R_\infty} J(r) r^{1+2m} dr$. Then, the **(approximate)** interaction Hamiltonian can be written as

$$\mathcal{H}_I(M) = \frac{1}{2} \int_{x \in \Omega} \sum_{m=1}^M (-1)^{m+1} S(m) \sum_{k=0}^m A(m; k, m-k) (D_1^k D_2^{m-k} \phi(x))^2. \quad (2.19)$$

Hence we have the following:

Proposition 3. *For $m, k \in \mathbb{N} \cup \{0\}$ and $m \geq k$, one has the identity*

$$A(m; k, m-k) = \frac{\pi}{2^{2m-1} m!} \frac{1}{k!(m-k)!}. \quad (2.20)$$

Proof. This simply follows from the trigonometric identity

$$\int_0^{2\pi} \cos^{2k_1} \theta \sin^{2k_2} \theta d\theta = \frac{(2k_1-1)!!(2k_2-1)!!}{(2k_1+2k_2)!!} \quad (2.21)$$

and the definition of $A(m; k, m-k)$ implies

$$\begin{aligned} A(m; k, m-k) &= \frac{1}{(2k)!(2(m-k))!} \int_0^{2\pi} (\cos \theta)^{2k} (\sin \theta)^{2(m-k)} d\theta \\ &= \frac{2\pi}{(2k)!(2(m-k))!} \frac{(2k-1)!!(2(m-k)-1)!!}{(2m)!!}. \end{aligned}$$

Since all of the odd numbers above will be cancelled by the full factorials in the denominator, we have the result.

Using the above result the **(approximate)** Hamiltonian in (2.19) can be written as

$$\mathcal{H}_I(M) = -\frac{1}{2} \int_{\Omega} dx \sum_{m=1}^M \tilde{c}_{2m} S(m) [\Delta^m \phi(x)] \phi(x) \quad (2.22)$$

where $\tilde{c}_{2m} := \frac{1}{(m!)^2} \frac{\pi}{2^{2m-1}}$, $S(m) := \int_0^\infty J(r) r^{2m+1} dr$ and $\Delta := D_{11} + D_{22}$ is the Laplace operator.

This can be seen by integrating (2.19) by parts k times over dx_1 , $m - k$ times over dx_2 , and using the fact that ϕ and all of its derivatives vanish on $\partial\Omega$. Then, one has

$$\begin{aligned}\mathcal{H}_I(M) &= -\frac{1}{2} \int_{\Omega} dx \sum_{m=1}^M \frac{\pi S(m)}{2^{2m-1} (m!)^2} \sum_{k=0}^m \frac{m!}{k!(m-k)!} [D_{11}^k D_{22}^{m-k} \phi(x)] \phi(x) \\ &= -\frac{1}{2} \int_{\Omega} dx \sum_{m=1}^M \tilde{c}_{2m} S(m) [\Delta^m \phi(x)] \phi(x).\end{aligned}\tag{2.23}$$

□

2.2.1 The Phase Field Equation

Using the functions $w(\phi)$ and $G(\phi)$ with properties discussed as above, we can write the **(approximate)** free energy as

$$\mathcal{F}_M[\phi] = \frac{1}{2} \int_{\Omega} \sum_{m=1}^M (-1)^{m+1} \tilde{c}_{2m} S(m) \sum_{k=0}^m \frac{m!}{k!(m-k)!} (D_1^k D_2^{m-k} \phi(x))^2 + W(\phi, u).\tag{2.24}$$

At equilibrium, the function ϕ minimizes the free energy yielding the equation

$$0 = \frac{\partial \mathcal{F}[\phi + \varepsilon \eta]}{\partial \varepsilon} \Big|_{\varepsilon=0}\tag{2.25}$$

where η is an arbitrary smooth function. To compute this quantity, we use the standard variational arguments below:

$$\begin{aligned}0 &= \frac{\partial \mathcal{F}_M[\phi + \varepsilon \eta]}{\partial \varepsilon} \Big|_{\varepsilon=0} \\ &= - \int_{\Omega} dx \sum_{m=1}^M \tilde{c}_{2m} S(m) \sum_{k=0}^m \frac{m!}{k!(m-k)!} \left(D_1^{2k} D_2^{2(m-k)} \phi \right) \eta + \frac{\partial \mathcal{F}_w[\phi + \varepsilon \eta]}{\partial \varepsilon} \Big|_{\varepsilon=0} \\ &= - \int_{\Omega} dx \left[\sum_{m=1}^M \tilde{c}_{2m} S(m) [(D_{11} + D_{22})^m \phi] + \int_{\Omega} dx D_1 W(\phi, u) \right] \eta.\end{aligned}\tag{2.26}$$

Since the integral must be zero for all smooth η , the integrand must vanish, leading to the identities:

$$0 = - \sum_{m=1}^M \tilde{c}_{2m} S(m) [(D_{11} + D_{22})^m \phi] + D_1 W(\phi, u)\tag{2.27}$$

where D_1 denotes differentiation with respect to the first variable. The S factor above is a quantity that depends on the integral of the interaction potential. It carries in it the information about microscopic length scale. In our analysis we shall treat it as a scaling factor from which one can get different distinguished limits.

For dynamic problems one can assume that the variational derivative of the free energy is proportional to the time derivative of the free energy functional. Hence the resultant equation would be

$$\tau\phi_t = - \sum_{m=1}^M \tilde{c}_{2m} S(m) \Delta^m \phi + \frac{w'(\phi)}{a} - Bu. \quad (2.28)$$

Thus, (2.28) is a generalization of the steady state phase field equation. Combining this with (1.5), we obtain the two coupled partial differential equations which we call generalized phase field equations.

2.2.2 Asymptotic Analysis

For the analysis, it is best to work with the local coordinates. Let Γ_t be the limit interface between two phases. Assuming that it is smooth we can parametrize it by arclength. Then, the location of a point near the limit interface can be described in the local coordinate system, (s, r) with the following transformation

$$x = X_0(s, t) + r\hat{n}(s, t) \quad (2.29)$$

where $r : r(x, t)$ is the signed distance from x to Γ_t , $\hat{n} = (\cos\theta, \sin\theta)$ is the unit normal, $s : s(x, t)$ is the arclength. It is also possible to use a stretched coordinate system by

$$x = x_0(s, t) + r\hat{n}(s, t) \quad (2.30)$$

We need to know how the partial derivatives transform to the new coordinate system. For the time derivative we have

$$\frac{df(r, s, t)}{dt} = \frac{\partial f}{\partial r} \frac{\partial r}{\partial t} + \frac{\partial f}{\partial s} \frac{\partial s}{\partial t} + \frac{\partial f}{\partial t} \quad (2.31)$$

Now, the $\frac{\partial r}{\partial t}$ term above can be written in terms of the velocity of the limit interface. Let us take the derivative of (2.30) with respect to time.

$$0 = \frac{\partial x_0}{\partial s} \frac{\partial s}{\partial t} + \frac{\partial x_0}{\partial t} + \frac{\partial r}{\partial t} \hat{n} + r \frac{\partial \hat{n}}{\partial s} \frac{\partial s}{\partial t} + r \frac{\partial \hat{n}}{\partial t} \quad (2.32)$$

multiplying this from right by \hat{n} , we find that the first, fourth and fifth terms on the RHS become zero and one is left with the equality

$$\frac{\partial r}{\partial t} = -v$$

where $v := \frac{\partial x_0}{\partial t} \cdot \hat{n}$ is the speed of the interface. Similarly the gradient of a function is given by

$$\nabla f = f_r \nabla r + f_s \nabla s$$

For ∇r , we use (2.30) with the convention that vectors are represented by row matrices and spatial operators are represented by column matrices. Then we have

$$I = \nabla s x_{0s} + \nabla r \hat{n} + r \nabla s \hat{n}_s \quad (2.33)$$

If we multiply this equation from right by \hat{n}^T , i.e., by the transpose of \hat{n} we find

$$\hat{n}^T = \nabla r \quad (2.34)$$

Similarly if we multiply (2.33) by τ^T , the unit tangent, then we have

$$\tau^T = \nabla s (1 + r \kappa(s))$$

since $\hat{n}_s = \kappa(s) \tau(s)$

2.2.3 The Stretched Variable

Let $\varphi = \varphi_\varepsilon$ be a solution of (3.3) and $\Gamma_t^\varepsilon := \{x \mid \varphi_\varepsilon(x, t) = 0\}$ be the zero level set of φ_ε . With respect to the ε -independent reference manifold Γ_t , we represent Γ_t^ε locally as

$$X_\varepsilon(s, t) := X_0(s, t) + \varepsilon H_\varepsilon(s, t)\mathbf{n}(s, t) \in \Gamma_t^\varepsilon,$$

where $\varepsilon H_\varepsilon$ admits an expansion $\varepsilon H_\varepsilon(s', t) = \varepsilon h_1(s, t) + \varepsilon^2 h_2(s, t) + \dots$. In this context, h_0 can be regarded as the unknown X_0 . The location of the interface Γ_t^ε is then uniquely determined by the coefficients X_0, h_1, h_2, \dots , of the asymptotic ε power series expansion of X_ε .

We introduce the stretched variable

$$z = Z(x, t) := \frac{r(x, t) - \varepsilon H_\varepsilon(s(x, t), t)}{\varepsilon} = \frac{r}{\varepsilon} - H_\varepsilon(s', t).$$

The relationship between the ε -dependent normal and \hat{n} is then

$$\begin{aligned} \hat{n}_\varepsilon &= \hat{n}(s, t) - \varepsilon \nabla H_\varepsilon(s(x, t), t) + O(\varepsilon^2) \\ &= \hat{n}(s, t) - \varepsilon H_{\varepsilon s} \nabla s + O(\varepsilon^2) \\ &= \hat{n}(s, t) - \varepsilon H_{\varepsilon s} \tau + O(\varepsilon^2) \end{aligned}$$

Now, since $\hat{n}(s) = (\cos \theta(s), \sin \theta(s))$. Then

$$\begin{aligned} n_\varepsilon &= (\cos \theta + \varepsilon H_{\varepsilon s} \sin \theta, \sin \theta - \varepsilon H_{\varepsilon s} \cos \theta) + O(\varepsilon^2) \\ &= (\cos(\theta - \varepsilon H_{\varepsilon s}), \sin(\theta - \varepsilon H_{\varepsilon s})) + O(\varepsilon^2) \end{aligned}$$

So n_ε is different than \hat{n} by a rotation of an angle at the order $O(\varepsilon)$. Using the above relations partial derivatives can be rewritten in the new coordinates system as

$$\begin{aligned} \varepsilon \frac{\partial}{\partial x_1} &= \cos \theta \frac{\partial}{\partial z} + \varepsilon H_{\varepsilon s} \sin \theta \frac{\partial}{\partial z} - \varepsilon \sin \theta \frac{\partial}{\partial s} + O(\varepsilon^2) \\ \varepsilon \frac{\partial}{\partial x_2} &= \sin \theta \frac{\partial}{\partial z} - \varepsilon H_{\varepsilon s} \cos \theta \frac{\partial}{\partial z} + \varepsilon \cos \theta \frac{\partial}{\partial s} + O(\varepsilon^2) \end{aligned} \tag{2.35}$$

From these one can show that

$$\varepsilon^2 \Delta = \partial_{zz} + \varepsilon \kappa \partial_z + O(\varepsilon^2) \tag{2.36}$$

where κ is the curvature.

Let the phase function defined in terms of the inner variable be denoted by

$$\Phi := \Phi(z, s, t; \varepsilon) \quad (2.37)$$

$\Phi(z, \theta, t)$ can be expanded formally in terms of ε as follows:

$$\Phi(z, \theta, t; \varepsilon) = \Phi^0(z, \theta, t) + \varepsilon \Phi^1(z, \theta, t) + \dots$$

where each Φ^i is independent of ε .

Then, higher order derivatives transform by

$$\varepsilon^k \varepsilon^{m-k} D_1^k \Phi D_2^{m-k} \Phi = \left\{ (\cos \theta)^k \frac{\partial^k \Phi}{\partial z^k} \right\} \left\{ (\sin \theta)^{m-k} \frac{\partial^{m-k} \Phi}{\partial z^{m-k}} \right\} + O(\varepsilon). \quad (2.38)$$

$$\varepsilon^{2m} \Delta^m \Phi = \frac{\partial^{2m} \Phi}{\partial z^{2m}} + m\kappa \varepsilon \frac{\partial^{2m-1} \Phi}{\partial z^{2m-1}} + O(\varepsilon^2).$$

Finally, before going into further calculations, we make the following scaling assumption on $S(m)$

$$S(m) \sim \frac{\varepsilon^{2m}}{a}. \quad (2.39)$$

In [22] the surface tension (in the way it was defined there) scales as $\sigma \sim \varepsilon/a$, so that for $a := \varepsilon$ one has $\sigma \sim O(1)$. Since σ (more properly, the associated capillarity length, $d_0 := \sigma/[s]_E$) is generally very small in comparison with the length scale of the experiment, the retention of the parameter a that can be made larger than ε can lead to consideration of a different distinguished limit.

With this scaling, upon multiplying by $a = \varepsilon$, the phase field equation through $O(\varepsilon)$ is given by

$$0 = - \sum_{m=1}^M \left[c_{2m} \frac{\partial^{2m}}{\partial z^{2m}} \Phi + m\kappa \varepsilon \frac{\partial^{2m-1}}{\partial z^{2m-1}} \Phi \right] + w'(\Phi) - aBu + O(\varepsilon^2) \quad (2.40)$$

where $S(m) = \alpha \varepsilon^{2m}/a$. Substituting the ε expansion for Φ , we write the phase field equation as

$$0 = - \sum_{m=1}^M \left[c_{2m} \frac{\partial^{2m}}{\partial z^{2m}} (\Phi^0 + \varepsilon \Phi^1) + m\kappa \varepsilon \frac{\partial^{2m-1}}{\partial z^{2m-1}} (\Phi^0 + \varepsilon \Phi^1) \right] + w'(\Phi^0 + \varepsilon \Phi^1) - aBu + O(\varepsilon^2). \quad (2.41)$$

Expanding the w' term using

$$w'(\Phi^0 + \varepsilon\Phi^1) = w'(\Phi^0) + \varepsilon w''(\Phi^0)\Phi^1 + \dots \quad (2.42)$$

one can write out the different orders in the differential equation above. Then, in the case $a := \varepsilon$, the $O(1)$ and $O(\varepsilon)$ equations become

$$0 = - \sum_{m=1}^M c_{2m} \frac{\partial^{2m}\Phi^0}{\partial z^{2m}} + w'(\Phi^0) \quad (2.43)$$

$$0 = - \sum_{m=1}^M c_{2m} \left[\frac{\partial^{2m}\Phi^1}{\partial z^{2m}} + m\kappa \frac{\partial^{2m-1}\Phi^0}{\partial z^{2m-1}} \right] + w''(\Phi^0)\Phi^1 - Bu. \quad (2.44)$$

Now multiplying (2.43) by $\partial\Phi^0/\partial z$ and integrate as follows:

$$\int_{-\infty}^{\rho} w'(\Phi^0) \frac{\partial\Phi^0}{\partial z} dz = \int_{-\infty}^{\rho} \sum_{m=1}^M c_{2m} \frac{\partial^{2m}\Phi^0}{\partial z^{2m}} \frac{\partial\Phi^0}{\partial z} dz. \quad (2.45)$$

Now, for any function ψ , the identity

$$\frac{\partial^{2m}\psi}{\partial z^{2m}} \frac{\partial\psi}{\partial z} = \frac{\partial}{\partial z} \left\{ \frac{(-1)^{m-1}}{2} \left(\frac{\partial^m\psi}{\partial z^m} \right)^2 + \sum_{k=1}^{m-1} (-1)^{k+1} \frac{\partial^{2m-k}\psi}{\partial z^{2m-k}} \frac{\partial^k\psi}{\partial z^k} \right\} \quad (2.46)$$

means that the left hand side of (2.46) is an exact differential, so (2.45) has the form

$$w(\Phi^0(z)) = \sum_{m=1}^M c_{2m} \left\{ \frac{(-1)^{m-1}}{2} \left(\frac{\partial^m\Phi^0}{\partial z^m} \right)^2 + \sum_{k=1}^{m-1} (-1)^{k+1} \frac{\partial^{2m-k}\Phi^0}{\partial z^{2m-k}} \frac{\partial^k\Phi^0}{\partial z^k} \right\} \quad (2.47)$$

since $w'(\pm 1) = 0$ and the derivatives of Φ^0 vanish at $-\infty$. Integrating this equation over $(-\infty, \infty)$ one has

$$\begin{aligned} \int_{-\infty}^{\infty} w(\Phi^0(z)) dz &= \sum_{m=1}^M c_{2m} \frac{(-1)^{m-1}}{2} \left\| \frac{\partial^m\Phi^0}{\partial z^m} \right\|^2 \\ &\quad + \sum_{k=1}^{m-1} (-1)^{k+1} (-1)^{m-k} \left\| \frac{\partial^m\Phi^0}{\partial z^m} \right\|^2 \\ &= \sum_{m=1}^M c_{2m} (-1)^{m-1} \left(m - \frac{1}{2} \right) \left\| \frac{\partial^m\Phi^0}{\partial z^m} \right\|^2 \end{aligned} \quad (2.48)$$

where integration by parts is used $m - 1$ times in the second set of integrals, and $\|\psi\|^2 := \int_{-\infty}^{\infty} |\psi|^2$.

Surface Tension

Now, we can write down an expression for the surface tension. The surface tension is understood by a local interpretation. Physically, local free energy is obtained by integrating the free energy density, F , over a small region (tube) across a small section of the interface minus the free energy of the bulk sides in the same region (tube). Since the system is isotropic, the solutions of the phase field equation is independent of the orientation. Then we define the surface tension as the integral of F along the line in the direction \hat{n}

$$\begin{aligned}\sigma &: = \int_{\hat{n}\mathbb{R}} \left(-(\Delta^{2n}\phi) \frac{\phi}{2} + W(\phi) \right) H^1(dx) \big|_{\phi(x)=\Phi^0(z,s)} \\ &= \int_{-\infty}^{\infty} \sum_{m=1}^M \left\{ \frac{(-1)^{m+1}}{2} c_{2m} \left(\frac{\partial^m \Phi^0}{\partial z^m} \right)^2 + w(\Phi^0) \right\}\end{aligned}$$

Later we will see that this definition is compatible with the interfacial free density that will be defined in the following sections. Then, using the identity (2.48), one has

$$\begin{aligned}\sigma &= \sum_{m=1}^M \frac{(-1)^{m+1}}{2} c_{2m} \left\| \frac{\partial^m \Phi^0}{\partial z^m} \right\|^2 + (-1)^m \frac{c_{2m}}{a} \left(m - \frac{1}{2} \right) \left\| \frac{\partial^m \Phi^0}{\partial z^m} \right\|^2 \\ &= \sum_{m=1}^M \left\{ (-1)^{m+1} c_{2m} m \left\| \frac{\partial^m \Phi^0}{\partial z^m} \right\|^2 \right\}\end{aligned}\tag{2.49}$$

Result 1. *For a stationary interface, in the limit $a, \varepsilon \rightarrow 0$, with the scaling $S(m) = \varepsilon^{2m}/a$ and $a = \varepsilon$, the phase field equations $\{(2.27), (1.5)\}$ have asymptotic solutions that satisfy the following sharp interface (Gibbs-Thomson) condition*

$$u[s]_E = -\kappa\sigma.$$

Derivation. To obtain the Gibbs-Thomson relation we need use the $O(\varepsilon)$ order phase field equation. Defining

$$L\Psi := \sum_{m=1}^M c_{2m} \frac{\partial^{2m}}{\partial z^{2m}} \Psi - w''(\Phi^0) \Psi$$

$$H := - \sum_{m=1}^M mc_{2m}\kappa \frac{\partial^{2m-1}}{\partial z^{2m-1}} \Phi^0 - Bu \quad (2.50)$$

we can write the $O(\varepsilon)$ equation as $L\Phi^1 = H$. Denoting $(f, g) := \int_{-\infty}^{\infty} fg$ we multiply both sides of $L\Phi^1 = H$ by $d\Phi^0/d\rho$ and integrate over the real line (treating u as a constant in this first order inner expansion):

$$\left(L\Phi^1, \frac{\partial}{\partial z} \Phi^0 \right) = \left(H, \frac{\partial}{\partial z} \Phi^0 \right). \quad (2.51)$$

Then by the Fredholm Alternative theorem, since $\partial\Phi^0/\partial z$ solves $L\Psi = 0$, we conclude that

$$0 = \left(H, \frac{\partial}{\partial z} \Phi^0 \right)$$

$$\begin{aligned} \int_{-\infty}^{\infty} Bu \frac{\partial}{\partial z} \Phi^0 dz &= \left(- \sum_{m=1}^M mc_{2m}\kappa \frac{\partial^{2m-1}}{\partial z^{2m-1}} \Phi^0, \frac{d}{dz} \Phi^0 \right) \\ (\Phi_+ - \Phi_-)Bu &= -\kappa \sum_{m=1}^M \int (-1)^{m-1} mc_{2m} (\Phi_m^0)^2 dz \end{aligned} \quad (2.52)$$

where, on the right hand side, we have used integration by parts $m - 1$ times. The right hand side of this equation is the curvature times the surface tension that was earlier. We claim that the left hand side is just the product of temperature and entropy difference per unit volume between the phases.

Indeed, from the free energy we can find the entropy difference per unit volume between the phases. Recalling the relation between the free energy and entropy density, s , and volume, V ,

$$s = -\frac{1}{V} \frac{\partial \mathcal{F}}{\partial u} \quad (2.53)$$

we obtain, upon performing this differentiation in each of the pure phases, the identity

$$[s]_E = \frac{1}{V} \left(\frac{-\partial \mathcal{F}[\Phi_+]}{\partial u} - \frac{-\partial \mathcal{F}[\Phi_-]}{\partial u} \right) = \frac{1}{V} \int_{\Omega} B(\Phi_+ - \Phi_-) dx dy = B(\Phi_+ - \Phi_-). \quad (2.54)$$

Hence we obtain the Gibbs-Thomson interface relation, (1.10).

Entropy Between Phases and the General Function $G(\phi, u)$

The function $G(\phi, u)$ represents the coupling of the phase field, ϕ , with the temperature, u . In general, its form will depend on microscopic details of the system. However, one can use different functions for G without altering the macroscopic conditions. So far, we have assumed the simplest form, i.e. $G(\phi, u) = B\phi u$ with $B := [s]_E/(\Phi_+ - \Phi_-)$. More generally, we can assume that $G(\Phi, u)$ has partial derivatives with respect to both variables and is linear in u .

2.3 BASIC COMBINATORIAL IDENTITIES FOR THE ANISOTROPIC PROBLEM

Here, we prepare the tools to be used in the next section, where we obtain the main results of this part. In the sequel, the interaction terms will be assumed to be directionally dependent, the angle which is defined with respect to the x_1 axis of the local coordinate system in $2 - d$.

To begin with, let us consider simple $2n - fold$ symmetric interactions in $2d$. Let $J(x_1, x_2)$ have the form

$$J(r, \theta) = J_c(r) \cos(2n\theta) + J_s(r) \sin(2n\theta)$$

In Section 2, we found the interaction Hamiltonian to be

$$\mathcal{H}_I = \sum_{m=0}^M \sum_{k_1+k_2=m} \int_{y \in \Omega} (-1)^{m+1} \frac{[D_1^{k_1} D_2^{k_2} \phi(y)]^2}{(2k_1)!(2k_2)!} \int_{x \in \Omega} x_1^{2k_1} x_2^{2k_2} J(x_1, x_2) \quad (2.55)$$

where k_1, k_2 are non-negative integers. Before evaluating this expression we define a key part of the Hamiltonian in the manner of the previous sub-section:

$$A_{ani}(m, n, k_1, k_2) := \frac{1}{(2k_1)!(2k_2)!} \int_0^{R_\infty} r^{2m+1} dr \int_0^{2\pi} J(r, \theta) \cos^{2k_1} \theta \sin^{2k_2} \theta d\theta. \quad (2.56)$$

With this definition, the Hamiltonian has the same similar form as in the isotropic case, namely,

$$\mathcal{H}_I = - \sum_{m=0}^M \int dy \sum_{2k_1+2k_2=2m} A_{ani}(m, n, k_1, k_2) [D_{11}^{k_1} D_{22}^{k_2} \phi(y)] \frac{\phi(y)}{2}. \quad (2.57)$$

which differs from the isotropic case in that the $\sum A_{ani}$ terms will not yield Laplacian operators to a power, but rather operators which are orientation dependent. To see this dependence more explicitly, we need the following lemmas.

Lemma 4. *For any $k_1, k_2, m := k_1 + k_2$, and n in \mathbb{N} we have the relations*

$$\begin{aligned} \int_0^{2\pi} \cos^{2k_1} \theta \sin^{2k_2} \theta \exp(i2n\theta) d\theta &= 0 \quad \text{if } m < n \\ &= \frac{(-1)^{k_2} \pi}{2^{2n-1}} \quad \text{if } m = n \\ &= \sum_{j_1+j_2=m+n} \pi \frac{C(2k_1, j_1) C(2k_2, j_2)}{(-1)^{j_2} (-1)^{k_2} 2^{2m-1}} \quad \text{if } m > n \end{aligned} \quad (2.58)$$

where $C(p, q) := \frac{p!}{(p-q)!q!}$.

Proof. (of Lemma)

(i) For $m < n$, the following integral vanishes:

$$\begin{aligned} T(m, n) &= \int_0^{2\pi} e^{2in\theta} \left(\frac{e^{i\theta} + e^{-i\theta}}{2} \right)^{2k_1} \left(\frac{e^{i\theta} - e^{-i\theta}}{2i} \right)^{2k_2} d\theta \\ &= 0 \end{aligned} \quad (2.59)$$

This occurs because, when we distribute the terms in the parentheses, each exponential term will have an exponent which add up to an integer less than m . Hence each of the integrals is identically zero, as $k_1 + k_2 = m < n$.

(ii) For $m = n$ the the same integral yields

$$\int \frac{e^{2in\theta}}{(-1)^{k_2} 2^{2m}} (\dots + e^{-i2k_1\theta} \dots + (-1)^{k_2} e^{-i2k_2\theta}) = \frac{(-1)^{k_2} \pi}{2^{2n-1}}, \quad (2.60)$$

since the only non-vanishing term occurs when $k_1 + k_2 = m = n$.

(iii) For $m = k_1 + k_2 = n + l$, the integral can be evaluated as follows:

$$T(m, n) = \int \frac{e^{2in\theta}}{(-1)^{k_2} 2^{2m}} (e^{i2k_1\theta} + \dots + C(2k_1, j_1) e^{-i(2k_1-j_1)\theta} \dots + e^{-i2k_1\theta}) \\ \cdot (e^{i2k_2\theta} + \dots (-1)^{j_2} C(2k_2, j_2) e^{-i(2k_2-j_2)\theta} + \dots e^{-i2k_2\theta}).$$

Since $m > n$, some of the integrals above will not vanish. Collecting the non-vanishing terms leads to the result,

$$\begin{aligned} T(m, n) &= \int_0^{2\pi} \frac{e^{2in\theta}}{2^{2m} (-1)^{k_2}} \sum_{j_1=0}^{2k_1} C(2k_1, j_1) e^{i2(k_1-j_1)\theta} \\ &\quad \cdot \sum_{j_2=0}^{2k_2} (-1)^{j_2} C(2k_2, j_2) e^{i2(k_2-j_2)\theta} \\ &= \frac{1}{2^{2m} (-1)^{k_2}} \sum_{j_1=0}^{2k_1} \sum_{j_2=0}^{2k_2} \int_0^{2\pi} C(2k_1, j_1) (-1)^{j_2} C(2k_2, j_2) e^{i2(m+n-j_1-j_2)\theta} \\ &= \frac{\pi}{2^{2m-1} (-1)^{k_2}} \sum_{j_1=0}^{2k_1} \sum_{j_2=0}^{2k_2} C(2k_1, j_1) (-1)^{j_2} C(2k_2, j_2) \delta_{m+n, j_1+j_2} \\ &= \frac{\pi}{2^{2m-1} (-1)^{k_2}} \sum_{j_1+j_2=m+n} C(2k_1, j_1) C(2k_2, j_2) (-1)^{j_2} \end{aligned} \quad (2.61)$$

which concludes the proof of Lemma 1. \square

Lemma 5. *Given an anisotropy of the form $J(r, \theta) = J_c(r) \cos 2n\theta + J_s(r) \sin 2n\theta$, for the principle sum, i.e., $P(m, n) := \sum_{2k_1+2k_2=2m} A_{ani}(m, n, k_1, k_2) D_{11}^{k_1} D_{22}^{k_2}$ we have the following identities for each of the three cases:*

(i) If $m < n$, then

$$P(m, n)\phi = 0. \quad (2.62)$$

(ii) If $m = n$, then

$$P(m, n)\phi = \frac{1}{(2n)! 2^{2n-1}} [S_c(n) \Re Re(D_1 + iD_2)^{2n}] \phi.$$

(iii) If $n < m = n + l$, then

$$P(m, n)\phi = \frac{C(2m, l)}{(2m)!2^{2m-1}}(D_{11} + D_{22})^l [S_c(n) \Re Re(D_1 + iD_2)^{2n}] \phi \quad (2.63)$$

where $S_c(m) := \int_0^\infty J_c(r) r^{2m+1} dr$.

As noted earlier, we assume that the interactions are either of finite range, or they decay sufficiently rapidly to ensure the convergence of the integrals.

Proof. (of Lemma)

We have three cases to consider

(i) The case $m < n$.

For $m < n$, the integral $\int_0^{2\pi} \cos^{2k_1} \theta \sin^{2k_2} \theta \exp^{2in\theta} d\theta$

vanishes by Lemma 3, implying immediately the identity

$$P(m, n)\phi = 0.$$

(ii) The case $m = n$.

Using Lemma 1 we have the identities:

$$\begin{aligned} P(m, n) &= \sum_{2k_1+2k_2=2m} \frac{D_{11}^{k_1} D_{22}^{k_2}}{(2k_1)!(2k_2)!} S_c(n) \int_0^{2\pi} \cos 2n\theta \cos^{2k_1} \theta \sin^{2k_2} \theta d\theta \\ &= \Re Re \sum_{2k_1+2k_2=2n} S_c(n) \frac{1}{(2n)!} C(2n, 2k_1) \frac{(-1)^{k_2} \pi}{2^{2n-1}} D_1^{2k_1} D_2^{2k_2} \phi \\ &= \frac{S_c(n) \pi}{(2n)! 2^{2n-1}} \Re Re[(D_1 + iD_2)^{2n}] \phi. \end{aligned} \quad (2.64)$$

(ii) The case $m > n$.

Using the identity $A_{ani}(m, n, k_1, k_2) = \frac{S_c(m)}{(2k_1)!(2k_2)!} \int e^{2in\theta} \cos^{2k_1} \theta \sin^{2k_2} \theta d\theta$, and

setting $D_1 = p$, $D_2 = q$, the principal sum is evaluated as

$$\begin{aligned} P(m, n)\phi &= \Re Re \sum_{2k_1+2k_2=2m} \frac{S_c(m)}{(2k_1)!(2k_2)!} \frac{\pi}{2^{2m-1} (-1)^{k_2}} \\ &\cdot \sum_{j_1+j_2=m+n} C(2k_1, j_1) C(2k_2, j_2) (-1)^{j_2} p^{2k_1} q^{2k_2} \phi. \end{aligned} \quad (2.65)$$

Define upper case J_1, J_2 as $J_1 := 2k_1 - j_1$ and $J_2 := 2k_2 - j_2$, so that

$$\begin{aligned}
P(m, n) &= \Re Re \sum_{2k_1+2k_2=2m} \frac{S_c(m)}{(2k_1)!(2k_2)!} \frac{\pi}{2^{2m-1}(-1)^{k_2}} \\
&\cdot \sum_{J_1+J_2=m-n} \frac{2k_1 \dots (2k_1 - J_1 + 1)}{J_1!} p^{2k_1} \frac{2k_2 \dots (2k_2 - J_2 + 1)}{J_2!} (-1)^{J_2} q^{2k_2} \\
&= \frac{S_c(m)\pi}{2^{2m-1}} \Re Re \sum_{2k_1+2k_2=2m} \frac{1}{(2k_1)!(2k_2)!(-1)^{k_2}} \\
&\cdot \sum_{J_1+J_2=m-n} \frac{p^{J_1}}{J_1!} \frac{\partial^{J_1}}{\partial p^{J_1}} (-1)^{J_2} \frac{q^{J_2}}{J_2!} \frac{\partial^{J_2}}{\partial q^{J_2}} p^{2k_1} q^{2k_2}. \tag{2.66}
\end{aligned}$$

Notice that, combinatorial factors in the second sum are written in terms of derivatives of polynomials. Next, we change the order of sums and take the derivatives outside of the $\sum_{2k_1+2k_2=2m}$ summation and multiplying and dividing by $(2m)!$ to obtain

$$\begin{aligned}
P(m, n)\phi &= \frac{S_c(m)\pi}{(2m)!2^{2m-1}} \Re Re \sum_{J_1+J_2=m-n} (-1)^{J_2} \left(\frac{p^{J_1}}{J_1!} \frac{\partial^{J_1}}{\partial p^{J_1}} \frac{q^{J_2}}{J_2!} \frac{\partial^{J_2}}{\partial q^{J_2}} \right) \\
&\cdot \sum_{2k_1+2k_2=2m} \frac{(2m)!}{(2k_1)!(2k_2)!} \frac{p^{2k_1} q^{2k_2} \phi}{(-1)^{k_2}}. \tag{2.67}
\end{aligned}$$

Now since the second sum is just the real part of binomial expansion of $(p + iq)^{2m}$ it will be easy to calculate the derivatives that we have moved outside of the sum:

$$\begin{aligned}
&= \frac{S_c(m)\pi}{(2m)!2^{2m-1}} \Re Re \sum_{J_1+J_2=m-n} (-1)^{j_2} \tag{2.68} \\
&\cdot \left(\frac{p^{J_1}}{J_1!} \frac{\partial^{J_1}}{\partial p^{J_1}} \frac{q^{J_2}}{J_2!} \frac{\partial^{J_2}}{\partial q^{J_2}} \right) (p + iq)^{2m} \phi \\
&= \frac{S_c(m)\pi}{(2m)!2^{2m-1}} \Re Re \sum_{J_1+J_2=m-n} (-1)^{J_2} \\
&\cdot \frac{p^{J_1}}{J_1!} \frac{\partial^{J_1}}{\partial p^{J_1}} (2m \dots 2m - J_2 + 1) \frac{q^{j_2} i^{j_2}}{j_2!} (p + iq)^{2m-J_2} \phi \\
&= \frac{S_c(m)\pi}{(2m)!2^{2m-1}} \Re Re \sum_{J_1+J_2=m-n} \frac{p^{J_1}}{J_1!} \frac{q^{J_2} (-i)^{J_2}}{J_2!} \\
&\cdot (2m \dots 2m - J_1 - J_2 + 1) (p + iq)^{2m-J_2-J_1} \phi.
\end{aligned}$$

Note that the exponent of $p + iq$ in the third line and the coefficient just before it is

$$2m - (J_1 + J_2) = 2m - (m - n) = m + n$$

which is independent of J_1 and J_2 . So these can be taken outside of the sum. After tidying up the terms we observe again that the sum is another binomial expansion:

$$\begin{aligned} &= \frac{S_c(m)\pi}{(2m)!2^{2m-1}} [2m \dots (m+n+1)] (p+iq)^{m+n} \sum_{J_1+J_2=m-n} \frac{p^{J_1}}{J_1!} \frac{q^{J_2}(-i)^{J_2}}{J_2!} \phi \\ &= \frac{S_c(m)\pi}{(2m)!2^{2m-1}} C(2m, m-n) (p+iq)^{m+n} (p-iq)^{m-n} \phi \\ &= \Re Re \frac{S_c(m)\pi}{(2m)!2^{2m-1}} C(2m, l) (D_1 + iD_2)^{2n} (D_{11} + D_{22})^l \phi. \end{aligned} \tag{2.69}$$

This completes the proof of Lemma. \square

Remark 6. *It was suggested in an earlier paper [21] that, for $2n - \text{fold}$ symmetric interactions, one should consider at least the n^{th} degree differential equation, for, in lower order derivative terms this anisotropy will vanish due to the averaging process. We have seen that the A_{ani} terms are directly involved in the free energy and phase field equation. Thus, Lemma 4 (i) provides some justification for this suggestion as there is no contribution of $2n - \text{fold}$ anisotropic effects in the lower degree differential equations.*

Remark 7. *One can define a new quantity $\tilde{c}_{2m,n}$ that generalizes the coefficient $\tilde{c}_{2m} := \frac{1}{(m!)^2} \frac{\pi}{2^{2m-1}}$ of the isotropic section*

$$\tilde{c}_{2m,n} = \frac{C(2m, m-n)\pi}{(2m)!2^{2m-1}} = \begin{cases} \frac{\pi}{(m!)^2 2^{2m-1}} & \text{when } n = 0 \\ \frac{\pi}{(2n)! 2^{2n-1}} & \text{when } m = n \end{cases}. \tag{2.70}$$

and observe that, when we truncate the sums at a finite M value, we are not losing much of the physics. Looking at the values of the $\tilde{c}_{2m,n}$ terms (for $m \geq 2$ and $n \geq 0$) which are the key parts of the coefficients of higher degree derivatives, we see that each subsequent term is roughly an order of magnitude smaller than the previous one:

$$\frac{\tilde{c}_{2(m+1),n}}{\tilde{c}_{2m,n}} = \frac{(2m)!}{(2(m+1))!} \frac{C(2(m+1), m+1-n)/2^{2(m+1)-1}}{C(2m, m-n)/2^{2m-1}} < \frac{1}{6}. \tag{2.71}$$

In fact, when m and n are large this ratio is much smaller, e.g., for $n = 2$ and $m = 4$ one this ratio is already $1/84$; when $m = 8$, $n = 6$ the ratio is $1/180$.

Finally, as we perform the asymptotic calculations in local coordinates, we only need the highest and second highest terms which correspond to $O(1)$ and $O(\varepsilon)$ terms in the expansion. The following lemma helps distinguish these terms.

Lemma 8. *In the local coordinates (z, s) , the differential operator $(D_1 + iD_2)^{2m}$ has the following expansion:*

$$\begin{aligned} \varepsilon^{2m} \text{Re}(D_1 + iD_2)^{2m} &= \cos(2m\theta) \frac{\partial^{2m}}{\partial z^{2m}} + \varepsilon \sin(2m\theta) H_{\varepsilon s}(s) \frac{\partial^{2m-1}}{\partial z^{2m-1}} - \\ &\quad \varepsilon(2m^2 - m)\kappa \cos(2m\theta) \frac{\partial^{2m-1}}{\partial z^{2m-1}} - \varepsilon 2m \sin(2m\theta) \frac{\partial^{2m}}{\partial s \partial z^{2m-1}} + O(\varepsilon^2) \end{aligned}$$

Proof. We prove the lemma by induction on powers j of $(D_1 + iD_2)^j$ by carefully expanding the terms. Below we show the process of retaining, in each step, the highest and second highest terms. Denoting the curvature by κ , one has for $j = 1$ and $j = 2$, the identities

$$\begin{aligned} \varepsilon(D_1 + iD_2) &= [(\cos \theta \partial_z + \varepsilon H_{\varepsilon s} \sin \theta \partial_z - \varepsilon \sin \theta \partial_s) + i(\sin \theta \partial_z - \varepsilon H_{\varepsilon s} \cos \theta \partial_z + \varepsilon \cos \theta \partial_s)] \phi + O(\varepsilon^2) \\ &= [\cos(\theta(s) - \varepsilon H_{\varepsilon s}) + i \cos(\theta(s) - \varepsilon H_{\varepsilon s})] \partial_z + \varepsilon [-\sin \theta + i \cos \theta] \partial_s + O(\varepsilon^2) \\ &= \exp(i\theta(s) - \varepsilon H_{\varepsilon s}) \partial_z + i\varepsilon \exp(i\theta) \partial_s + O(\varepsilon^2) \end{aligned}$$

$$\begin{aligned} \varepsilon^2(D_1 + iD_2)^2 \phi &= \left(e^{i(\theta - \varepsilon H_{\varepsilon s})} \frac{\partial}{\partial z} + \varepsilon i e^{i\theta} \frac{\partial}{\partial s} \right) (e^{i(\theta - \varepsilon H_{\varepsilon s})} \phi_z + \varepsilon i e^{i\theta} \phi_s) + O(\varepsilon^2) \\ &= (e^{2i\theta - 2\varepsilon H_{\varepsilon s}} \phi_{zz} + \varepsilon 2i e^{i2\theta} \phi_{zs} + \varepsilon \kappa i^2 e^{2i\theta} \phi_z) + O(\varepsilon^2) \end{aligned} \quad (2.72)$$

where we used $\theta'(s) = \kappa(s)$. By the induction hypothesis, suppose the identity is true for $j = 2m - 1$, that is,

$$\begin{aligned} \varepsilon^{2m-1} (D_1 + iD_2)^{2m-1} \phi &= e^{i(2m-1)(\theta - \varepsilon H_{\varepsilon s})} \frac{\partial^{2m-1} \phi}{\partial z^{2m-1}} + \varepsilon (2m-1) i e^{i(2m-1)\theta} \frac{\partial^{2m-1} \phi}{\partial s \partial z^{2m-2}} \\ &\quad - \varepsilon \frac{((2m-1)^2 - (2m-1))}{2} \kappa e^{i(2m-1)\theta} \frac{\partial^{2m-2} \phi}{\partial z^{2m-2}} + O(\varepsilon^2) \end{aligned}$$

Applying the $\varepsilon(D_1 + iD_2)$ one more time to the above expression yields

$$\begin{aligned}
&= \left(e^{i(\theta - \varepsilon H_{\varepsilon s})} \frac{\partial}{\partial z} + i e^{i\theta} \frac{\partial}{\partial s} \right) (D_1 + iD_2)^{2m-1} \phi \\
&= e^{i2m(\theta - \varepsilon H_{\varepsilon s})} \frac{\partial^{2m} \phi}{\partial z^{2m}} + (2m-1) i e^{2im\theta} \frac{\partial^{2m} \phi}{\partial s \partial r^{2m-1}} \\
&\quad - \frac{((2m-1)^2 - (2m-1))}{2} e^{2mi\theta} \frac{\partial^{2m-1} \phi}{\partial z^{2m-1}} \\
&\quad - (2m-1) \kappa e^{2mi\theta} \frac{\partial^{2m-1} \phi}{\partial z^{2m-1}} + e^{2mi\theta} \frac{\partial^{2m} \phi}{\partial s \partial z^{2m-1}} + O(\varepsilon^2) \\
&= \left(e^{i2m\theta} \frac{\partial^{2m} \phi}{\partial z^{2m}} - (2m^2 - m) \kappa e^{2im\theta} \frac{\partial^{2m-1} \phi}{\partial z^{2m-1}} + 2mi \kappa e^{2mi\theta} \frac{\partial^{2m} \phi}{\partial s \partial z^{2m-1}} \right) + O(\varepsilon^2)
\end{aligned} \tag{2.73}$$

The proof is complete. \square

2.4 ANISOTROPIC INTERFACE CONDITIONS

The main conclusions of this part of our thesis are the Results 2 and 3 below. Although Result 3 is more general than Result 2, we think Result 2 is interesting since the anisotropy originates solely from the microscopic parameters but not from the solution of the equations. However, in Result 2 interactions are assumed to be purely $(2n - fold)$ symmetric which may lead to physically unrealistic situations. One manifestation is that the surface tension becomes negative for some values of θ . On the other hand, in Result 3, the conclusions are more general, but directional dependence of phase function must be taken into account.

2.4.1 Purely Anisotropic Case

In this section, we seek solutions that represent stationary planar interfaces at the melting temperature. For this purpose, we assume that $u \equiv 0$.

Recall now the interaction Hamiltonian

$$\mathcal{H}_I(N) = - \sum_{m=1}^N \sum_{k_1+k_2=m} \int_{y \in \Omega} \frac{[D_{11}^{k_1} D_{22}^{k_2} \phi(y)]}{(2k_1)!(2k_2)!} \frac{\phi(y)}{2} \int_{\Omega} x_1^{2k_1} x_2^{2k_2} J(x_1, x_2) dx_1 dx_2.$$

By Lemma 3 and Lemma 6, the free energy can be written in the new form

$$\mathcal{F}_N = \int_{\Omega} - [\varepsilon^{2n-1} \tilde{c}_{2n,n} [J_c(n) \Re Re(D_1 + iD_2)^{2n}] \frac{\phi}{2} + \frac{w(\phi)}{a} - G(\phi)u. \quad (2.74)$$

where $S_c(n) = J_c(n)\varepsilon^{2n}/\varepsilon$. Note that all lower order derivative terms are zero because of these lemmas. Then, Euler-Lagrange equations yields the desired phase field equation,

$$0 = - [\varepsilon^{2m} J_c(n) c_{2n,n} [\Re Re(D_1 + iD_2)^{2n} \phi] + w'(\phi) - aG'(\phi)u. \quad (2.75)$$

Asymptotic Expansion For the Phase Field Equation

Using the local coordinates (z, s, t) we denote the phase field

$$\varphi_{\varepsilon}(x, t) = \Phi(z, s, t) \quad x = X_0(s, t) + \varepsilon[z + H_{\varepsilon}(s, t)] \mathbf{n}(s, t).$$

Then, using the last lemma of the previous section, the differential equation (2.75) can be written as ($\tilde{c}_{2n,n} = J_c(n)c_{2n,n}$)

$$\begin{aligned} 0 = & -a\tilde{c}_{2n,n} \left(\cos 2n\theta \frac{\partial^{2n}}{\partial z^{2n}} + \varepsilon \sin(2m\theta) H_{\varepsilon s}(s) \frac{\partial^{2m-1}}{\partial z^{2m-1}} - \kappa \cos 2n\theta (2n^2 - n) \frac{\partial^{2n-1}}{\partial z^{2n-1}} \right) \Phi \\ & - a\tilde{c}_{2n,n} \left(2n\kappa(-\sin 2n\theta) \frac{\partial^{2n}\Phi}{\partial \theta \partial z^{2n-1}} \right) + w'(\Phi) - aG'(\Phi)u + O(\varepsilon^2) \end{aligned} \quad (2.76)$$

For brevity we define the “tension parameters” χ_{An} , χ_{Bn} and χ_{Cn} as

$$\begin{aligned} \chi_{An}(\theta)^{2n} &:= \tilde{c}_{2n,n}(\cos 2n\theta) \\ \chi_{Bn}(\theta)^{2n} &:= \tilde{c}_{2n,n}(2n^2 - n)(\cos 2n\theta) \\ \chi_{Cn}(\theta)^{2n} &:= \tilde{c}_{2n,n}2n(\sin 2n\theta) \end{aligned} \quad (2.77)$$

Next, we expand Φ in terms of the small parameter ε ,

$$\Phi(z, s) = \Phi^0(z, s) + \varepsilon\Phi^1(z, s) + \dots \quad (5.7a)$$

$$W'(\Phi^0 + \varepsilon\Phi^1) = w'(\Phi^0) + \varepsilon w''(\Phi^0)\Phi^1 + \dots$$

Then, we write out the different orders in ε for (2.76). To $O(1)$ we have,

$$0 = -\chi_{An}^{2n} \frac{\partial^{2n}\Phi^0}{\partial z^{2n}} + w'(\Phi^0). \quad (2.78)$$

Surface Tension

The surface tension is again defined as the integral of F along the line in the direction \hat{n}

$$\begin{aligned}\sigma(\hat{n}) &= \bar{\sigma}(\theta) := \int_{\hat{n}\mathbb{R}} \left(-\Re Re(D_1 + D_2)^{2n} \phi \frac{\phi}{2} + W(\phi) \right) H^1(dx) \big|_{\phi(x)=\Phi^0(z(x),s(x))} \\ &= \int_{\mathbb{R}} \left[-\frac{\chi_{An}^{2n}}{2} \cos(2n\theta) Q_{2nz} + W(Q) \right] dz\end{aligned}$$

Then, doing calculations in the manner of Section 2.2, we find it as

$$\sigma = n\chi_{An}^{2n}(-1)^{n+1} \int \left(\frac{\partial^n \Phi^0}{\partial z^n} \right)^2 dz$$

We also see from (2.78) that, for the operator defined by

$$L\Psi := \left[-\chi_{An}^{2n} \frac{\partial^{2n}}{\partial z^{2n}} + w''(\Phi^0) \right] \Psi,$$

we have

$$L\Phi_z = 0 \quad \text{and} \quad L\Phi_s = (\chi_{Cn})^{2n} \frac{\partial^{2n} \Phi^0}{\partial z^{2n}}. \quad (2.79)$$

Yet another observation here is that the above equation can be re-scaled by one parameter $\rho = z/\chi_{An}$ only. The derivatives are related by

$$\frac{\partial^n \Phi^0(z, \theta)}{\partial z^n} = \frac{1}{\chi_{An}^n} \left(\frac{\partial^n \varphi^0}{\partial \rho^n} \right).$$

where $\Phi^0(z) = \varphi^0(z/\chi_{An})$. Therefore, we can write the $O(1)$ phase field equation as simply

$$0 = -\frac{\partial^{2n} \varphi^0}{\partial \rho^{2n}} + w'(\varphi^0), \quad (2.80)$$

Therefore the surface tension can be written as

$$\sigma = n\chi_{An}^{2n}(-1)^{n+1} \int \left(\frac{\partial^n \Phi^0}{\partial z^n} \right)^2 dz = (-1)^{n+1} \chi_{An} \int_{-\infty}^{\infty} \left(\frac{\partial \varphi^0}{\partial \rho^n} \right)^2 d\rho.$$

A delicate point here is that the phase function is angle dependent as are the χ_n s. However, the new integral above is independent of angle because, φ^0 is exactly the solution of (2.80). So the θ dependence arises solely from the χ_{An} term.

The Default Correction and the Solvability Condition.

Because of our choice of an ε -independent chart there is an extra term in our phase field equation, i.e., $\varepsilon \sin(2m\theta) H_{\varepsilon s}(s) \frac{\partial^{2m-1} \Phi^0}{\partial z^{2m-1}}$. We can get rid of it by subtracting $\varepsilon \sin(2m\theta) Q$ from Φ^0 , i.e.,

$$\begin{aligned}\Phi(z, s, t) &= \Phi_s^0(z, s, t) - \varepsilon \Phi_s^0(z, s, t) + \varepsilon \hat{\Phi} + \dots \\ \hat{\Phi} &= \hat{\Phi}^1 + \varepsilon \hat{\Phi}^2 + \dots\end{aligned}\tag{2.81}$$

Then using (2.81), (2.79) and Lemma 4 we get

$$L\hat{\Phi}^1 = - \left(-\kappa \chi_{Bn}^{2n} \frac{\partial^{2n-1} \Phi^0}{\partial z^{2n-1}} - \chi_{Cn}^{2n} \frac{\partial^{2n} \Phi^0}{\partial z^{2n-1} \partial s} \right) - G'(\Phi^0)u$$

Since $\Psi = d\Phi^0/dz$ solves $L\Psi = 0$, one has by the Fredholm Alternative Theorem,

$$\left(L\hat{\Phi}^1, \frac{\partial \Phi^0}{\partial z} \right) = 0.$$

Using $\Phi^0(z) = \varphi^0(z/\chi_{An})$ we get

$$\begin{aligned}\int_{-\infty}^{\infty} -G'(\Phi^0)u \frac{\partial \Phi^0}{\partial z} dz &= \left(-\kappa \chi_{Bn}^{2n} \frac{\partial^{2n-1} \Phi^0}{\partial z^{2n-1}} - \chi_{Cn}^{2n} \frac{\partial^{2n} \Phi^0}{\partial z^{2n-1} s \partial \theta} \Phi^0, \frac{d}{dz} \Phi^0 \right) \\ \int_{-\infty}^{\infty} -G'(\Phi^0)u \frac{\partial \Phi^0}{\partial z} dz &= \kappa \left(-\frac{\chi_{Bn}^{2n}}{\chi_{An}^{2n-1}} \frac{\partial^{2n-1} \varphi^0}{\partial \rho^{2n-1}}, \frac{\partial \varphi^0}{\partial \rho} \right) \\ &\quad + \left(-\chi_{Cn}^{2n} \frac{\partial}{\partial \theta} \frac{1}{\chi_{An}^{2n-1}} \frac{\partial^{2n-1} \varphi^0}{\partial \rho^{2n-1}}, \frac{\partial \varphi^0}{\partial \rho} \right) \\ -[G(\Phi_+^0) - G(\Phi_-^0)]u &= (-1)^n \kappa \left(\frac{\chi_{Bn}^{2n}}{\chi_{An}^{2n-1}} + \frac{\chi_{Cn}^{2n}}{2} \frac{\partial}{\partial \theta} \frac{1}{\chi_{An}^{2n-1}} \right) \int_{-\infty}^{\infty} \left(\frac{\partial^n}{\partial \rho^n} \varphi^0 \right)^2 d\rho.\end{aligned}\tag{2.82}$$

Recalling the definition of χ_{An}^{2n} in (2.77) we compute the derivatives of χ_{An} as:

$$\frac{\partial}{\partial \theta} \chi_{An} = \frac{n \tilde{c}_{2n,n} (-\sin 2n\theta)}{n \chi_{An}^{2n-1}}\tag{2.83}$$

$$\frac{\partial^2}{\partial \theta^2} \chi_{An} = -2n \tilde{c}_{2n,n} \frac{(\cos 2n\theta)}{\chi_{An}^{2n-1}} + \frac{n \tilde{c}_{2n,n}}{n} (-\sin 2n\theta) \frac{\partial}{\partial \theta} \frac{1}{\chi_{An}^{2n-1}}.\tag{2.84}$$

So, comparing the expressions from surface tension and solvability, we conclude

$$\kappa(\sigma + \sigma_{\theta\theta}) = \kappa(-1)^{n+1} n (\chi_{An} + \chi_{An}''') \int_{-\infty}^{\infty} \left(\frac{\partial \varphi^0}{\partial \rho} \right)^2 d\rho = -[s]_{Eu}\tag{2.85}$$

Hence, we have actually derived the following result

Result 2. Let $J(r, \theta) = J_c(r) \cos 2n\theta + J_s(r) \sin 2n\theta$ be the strength of local interactions between atoms such that $J(r, \theta)$ is either of finite range or decays sufficiently rapidly with increasing r as discussed in Section 2. Consider a stationary interface in the limit $a, \varepsilon \rightarrow 0$ with the following scaling: $a = \varepsilon$, $S_c(n) = J_c(n)\varepsilon^{2n}/a$, $S_s(n) = J_s(n)\varepsilon^{2n}/a$. Formal asymptotic solutions to the $2n^{\text{th}}$ degree phase field equations (below) satisfy the Gibbs-Thomson-Herring interface condition:

$$\kappa(\sigma + \sigma_{\theta\theta}) = -[s]_E u. \quad (2.86)$$

2.4.2 General Anisotropy

A more general form of anisotropy has the form

$$J(r, \theta) = f(r) \sum_{n=0}^N [J_c(n) \cos 2n\theta + J_s(n) \sin 2n\theta].$$

1 displays simple example of such anisotropy, described by

$$g(\theta) = 10 + \cos(4\theta) + \frac{1}{3} \cos(16\theta) + \frac{1}{30} \cos(64\theta).$$

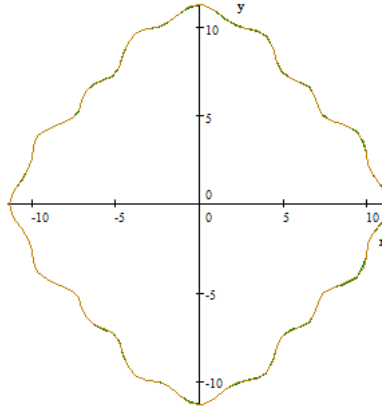


Figure 1: Example of Anisotropy for $J(r, \theta)$

We begin our treatment by writing the Hamiltonian in its general form, as obtained in (2.55) ,

$$\mathcal{H}_I(M) = \sum_{m=1}^M \sum_{k_1+k_2=m} \int_{y \in \Omega} (-1)^{m+1} \frac{[D_1^{k_1} D_2^{k_2} \phi(y)]^2}{(2k_1)!(2k_2)!} \int_{x \in \Omega} x_1^{2k_1} x_2^{2k_2} J(x_1, x_2) dx_1 dx_2$$

where M can be taken any integer with $M > N$. It is preferable to work with the other equivalent form of the Hamiltonian,

$$\begin{aligned} \mathcal{H}_I(M) = & - \sum_{m=1}^M \sum_{k_1+k_2=m} \int_{y \in \Omega} dy \frac{[D_{11}^{k_1} D_{22}^{k_2} \phi(y)]}{(2k_1)!(2k_2)!} \frac{\phi(y)}{2} \\ & \cdot \int_{x \in \Omega} d\theta f(r) r^{2m+1} dr \sum_{n=0}^N (J_c(n) \cos 2n\theta + J_s(n) \sin 2n\theta) \end{aligned} \quad (2.87)$$

We can take the $\sum_{n=0}^N$ summation outside the integration sign and change the order of summation, as the sums are finite. Then we employ Lemmas 3 and Lemma 6 of the previous section to express the Hamiltonian as

$$\begin{aligned} \mathcal{H}_I(M) = & - \sum_{m=1}^M \sum_{k_1+k_2=m} \int_{y \in \Omega} \frac{[D_{11}^{k_1} D_{22}^{k_2} \phi]}{(2k_1)!(2k_2)!} \frac{\phi}{2} \\ & \cdot \sum_{n=0}^N \int_{x \in \Omega} x_1^{2k_1} x_2^{2k_2} f(r) (J_c(n) \cos 2n\theta + J_s(n) \sin 2n\theta) \\ = & \int_{y \in \Omega} \sum_{m=1}^M \sum_{n=0}^m \tilde{c}_{2m,n} S(m) (D_{11} + D_{22})^{m-n} [\Re Re(D_1 + iD_2)^{2n} \phi] \frac{\phi}{2} \end{aligned} \quad (2.88)$$

where $S(m) = \int f(r) r^{2m+1} dr$. Note that in the last line, the second sum terminates as m due to the vanishing of the terms for $m < n$. From equation (2.88) we can easily write down the free energy (Euler-Lagrange equations) and the phase field equation as

$$\begin{aligned} \mathcal{F}_M = & - \int \sum_{m=1}^M \sum_{n=0}^m \tilde{c}_{2m,n} S(m) (D_{11} + D_{22})^{m-n} [\Re Re(D_1 + iD_2)^{2n} \phi] \frac{\phi}{2} \\ & + \frac{w(\phi)}{a} - G(\phi)u \end{aligned} \quad (2.89)$$

$$0 = - \sum_{m=1}^M \sum_{n=0}^m a \tilde{c}_{2m,n} S(m) (D_{11} + D_{22})^{m-n} [\Re Re(D_1 + iD_2)^{2n} \phi] \phi \quad (2.90)$$

$$+ w'(\phi) - aG'(\phi)u. \quad (5.23)$$

As before, we can express the $O(1)$ differential equation and the surface tension in local coordinates with $\tilde{c}_{2m,n} := c_{2m,n} J_c(n)$ and the scaling $S(m) \sim \varepsilon^{2m-1}$ yielding

$$0 = -\frac{\partial^{2m}\Phi^0}{\partial z^{2m}} \left(\sum_{n=0}^m \tilde{c}_{2m,n} \cos 2n\theta \right) + w'(\Phi) \quad (2.91)$$

$$\sigma = \int dz \sum_{m=1}^M f_0(-1)^{m+1} m \left(\frac{\partial^m \Phi^0}{\partial z^m} \right)^2 \sum_{n=0}^m \tilde{c}_{2m,n} \cos 2n\theta. \quad (2.92)$$

$$= \int dz \sum_{m=1}^M \frac{(\chi_{Am}^{2m})}{2} \frac{\partial^{2m}\Phi^0}{\partial z^{2m}} \Phi^0 + \int dz W(\Phi^0) \quad (2.93)$$

Once again we defined

$$\bar{\chi}_{Am}(\theta) := \left[\sum_{n=0}^m \tilde{c}_{2m,n} \cos 2n\theta \right]^{1/2m}.$$

Next, we derive the solvability condition by writing the $O(\varepsilon)$ phase field equation. Similarly to our proof in the pure anisotropic case (2.79) we get rid of the extra term by subtracting it out from the zeroth order solution, i.e.,

$$\begin{aligned} \Phi(z, s, t) &= \Phi_s^0(z, s, t) - \varepsilon \Phi_s^0(\mathbf{z}, s, t) + \varepsilon \hat{\Phi} + \dots \\ \hat{\Phi} &= \hat{\Phi}^1 + \varepsilon \hat{\Phi}^2 + \dots \end{aligned} \quad (2.94)$$

Then we obtain

$$\begin{aligned} 0 &= \sum_{m=1}^M \left\{ -\bar{\chi}_{Am}^{2m} \frac{\partial^{2m}}{\partial z^{2m}} + w''(\Phi^0) \right\} \varepsilon \hat{\Phi}^1 - \\ &\quad \left[-\varepsilon \kappa \bar{\chi}_{Bm}^{2m} \frac{\partial^{2m-1}}{\partial z^{2m-1}} - \varepsilon \kappa \bar{\chi}_{Cm}^{2m} \frac{\partial^{2m}}{\partial z^{2m-1} \partial s} \right] \Phi^0 \} - \varepsilon G'(\Phi^0) u \end{aligned} \quad (2.95)$$

where $\varepsilon_{Bm}^{2m}, \varepsilon_{Cm}^{2m}$ are defined in a similar fashion as follows:

$$\begin{aligned} \bar{\chi}_{Bm}^{2m} &:= \left[\sum_{n=0}^m \tilde{c}_{2m,n} (2n^2 - m) \cos 2n\theta \right] \\ \bar{\chi}_{Cm}^{2m} &:= \left[\sum_{n=0}^m 2n \tilde{c}_{2m,n} \sin 2n\theta \right]. \end{aligned}$$

We again define the operators

$$L\Psi := \sum_{m=1}^M \left[-\bar{\chi}_{Am}^{2m} \frac{\partial^{2m}\Phi^0}{\partial z^{2m}} + W''(\Phi^0) \right] \Psi \quad (2.96)$$

$$H := \sum_{m=1}^M - \left[-\kappa \bar{\chi}_{Bm}^{2n} \frac{\partial^{2m-1}}{\partial z^{2m-1}} - \bar{\chi}_{Cm}^{2m} \frac{\partial^{2m}}{\partial z^{2m-1} \partial s} \right] \Phi^0 - G'(\Phi^0)u. \quad (2.97)$$

Notice that, equation (2.97) has almost the same form as the pure (single mode) case, the difference being due to $\bar{\chi}_{Bm}^{2n}$ and $\bar{\chi}_{Cm}^{2n}$. Then, by the Fredholm theorem we have

$$\left(L\hat{\Phi}^1, \frac{\partial}{\partial z}\Phi^0 \right) = \left(H, \frac{\partial}{\partial z}\Phi^0 \right) = 0$$

since $d\Phi^0/d\rho$ solves $L\Psi = 0$. Letting $\Phi^0(z, s) = \varphi(z, \theta)$ we find that

$$\begin{aligned} - \int_{-\infty}^{\infty} G'(\Phi^0)u\Phi_z^0 dz &= \sum_{m=1}^M \kappa \left(\int_{-\infty}^{\infty} -\bar{\chi}_{Bm}^{2m} \frac{\partial^{2m-1}}{\partial z^{2m-1}} \varphi^0, \varphi_z^0 \right) \\ &\quad + \sum_{m=1}^M \kappa \left(-\bar{\chi}_{Cm}^{2m} \int_{-\infty}^{\infty} \frac{\partial^{2m}\varphi^0}{\partial z^{2m-1} \partial \theta}, \varphi_z^0 \right) \\ [G'(\phi_+^0) - G'(\phi_-^0)]u &= \sum_{m=1}^M -\kappa(-1)^{m+1} \int_{-\infty}^{\infty} \left(\bar{\chi}_{Bm}^{2m} + \bar{\chi}_{Cm}^{2m} \frac{1}{2} \frac{\partial}{\partial \theta} \right) \left(\frac{\partial^m \varphi^0}{\partial z^m} \right)^2 dz. \end{aligned} \quad (2.98)$$

Now we will compare the right hand side of the equation in the last row with the surface stiffness, i.e., $\sigma + \sigma_{\theta\theta}$. From equation (2.92)

$$\sigma = \int dz \sum_{m=1}^M -\frac{(\chi_{Am}^{2m})}{2} \frac{\partial^{2m}\varphi^0}{\partial z^{2m}} \varphi^0 + \int dz W(\Phi^0)$$

We note that the operator $\partial/\partial\theta$ acts on both the integral and $\bar{\chi}_{Ai}^{2m}$. Hence, there will be extra terms which were absent in the previous calculation.

$$\begin{aligned} \sigma_{\theta} &= - \int dz \sum_{m=1}^M \frac{(\chi_{Am}^{2m})'}{2} \frac{\partial^{2m}\varphi^0}{\partial z^{2m}} \varphi^0 - \int dz \sum_{m=1}^M (\chi_{Am}^{2m}) \frac{\partial^{2m}\varphi^0}{\partial z^{2m}} \varphi_{\theta}^0 + \int dz W'(\varphi^0) \varphi_{\theta}^0 \\ &= - \int dz \sum_{m=1}^M \frac{(\chi_{Am}^{2m})'}{2} \frac{\partial^{2m}\varphi^0}{\partial z^{2m}} \varphi^0 \end{aligned}$$

Above, the second and third term added up to zero by the rescaled $O(1)$ equation. The second derivative with respect to θ yields

$$\sigma_{\theta\theta} = - \int dz \sum_{m=1}^M \frac{(\chi_{Am}^{2m})''}{2} \frac{\partial^{2m} \varphi^0}{\partial z^{2m}} \varphi^0 - \int dz \sum_{m=1}^M (\chi_{Am}^{2m})' \frac{\partial^{2m} \varphi^0}{\partial z^{2m}} \varphi_\theta^0$$

Now, observe that

$$\begin{aligned} (\chi_{Am}^{2m})' &= - \sum_{n=0}^m 2f_0 n \tilde{c}_{2m,n} J_c(n) \sin 2n\theta = -(\chi_{Cm}^{2m})' \\ (\chi_{Am}^{2m})'' &= - \sum_{n=0}^m f_0 \tilde{c}_{2m,n} (4n^2) J_c(n) \cos 2n\theta \end{aligned}$$

Hence

$$\begin{aligned} (\sigma + \sigma_{\theta\theta}) \kappa &= \kappa \int_{-\infty}^{\infty} \bar{\chi}_{Bm}^{2m} \frac{\partial^{2m} \varphi^0}{\partial z^{2m}} \varphi^0 + \kappa \int_{-\infty}^{\infty} \bar{\chi}_{Bm}^{2m} \frac{\partial^{2m-1} \varphi^0}{\partial z^{2m-1}} \varphi_\theta^0 \\ &= (G(\Phi_+^0) - G(\Phi_-^0))u = -u[s]_E \end{aligned}$$

Thus we have proved the following

Result 3. *Let*

$$J(r, \theta) = f(r) \left[J_0 + \delta \sum_{n=1}^N \{ J_c(n) \cos(2n\theta) + J_s(n) \sin(2n\theta) \} \right]$$

satisfy the same conditions as in Result 1. Consider a stationary interface in the limit $\varepsilon, a \rightarrow 0$ with the scaling $a = \varepsilon$. Then formal asymptotic solutions to the phase field equations $\{(2.27), (1.5)\}$ satisfy the Gibbs-Thomson-Herring interface condition

$$-u[s]_E = \kappa(\sigma + \sigma'').$$

The result can be summarized as follows. One can start from a quite complicated anisotropy in terms of the microscopic interactions, and calculate the surface tension from the phase field equation. In the limit of a sharp interface one recovers the classical macroscopic results.

2.4.3 Non Equilibrium Systems

In the previous sections we assumed the interface to be stationary for the sake of clarity and simplicity. With a little more effort we can extend our discussion to non-equilibrium anisotropic systems. For a moving interface, the time derivative of the phase field, and therefore the left hand side of the phase field equation, will no longer be zero. This part of the equation is handled in the same manner as [20]. Then the time derivative of the phase function is

$$\tau\phi_t = -\frac{v\tau}{\varepsilon}\frac{\partial\Phi}{\partial z} + \tau\frac{\partial\Phi}{\partial s}\frac{\partial s}{\partial t} + \tau\frac{\partial\Phi}{\partial t}.$$

Using these dynamical relations we can derive the most general anisotropic phase field equations and derive the associated interface relation. The latent heat condition across the interface and the heat equation in the bulk phases (1.1) follow easily as shown in previous papers.

Result 4. *Let $J(r, \theta) = J_0 + \delta \sum_{n=0}^N \{J_c(n, r) \cos \theta + J_s(n, r) \sin \theta\}$ where δ is a parameter. Then the phase field equations are derived as*

$$\rho cu_t + \frac{l}{2}\phi_t = K\Delta u$$

$$\begin{aligned} \tau\phi_t = & -\sum_{m=1}^M aS(m)\tilde{c}_{2m,0}J_0(D_{11} + D_{22})^m\phi + w'(\phi) - aG'(\phi)u \\ & -\delta\sum_{m=1}^M\sum_{n=1}^m aS(m)\tilde{c}_{2m,n}(D_{11} + D_{22})^{m-n}[J_c(n)\Re Re(D_1 + iD_2)^{2n}]\phi. \end{aligned} \quad (2.99)$$

in the limit $\tau, a \rightarrow 0$ with the scaling $a = \varepsilon$, $\tau = \varepsilon^2$, formal asymptotic solutions satisfy the macroscopic condition

$$-u[s]_E = \kappa(\sigma + \sigma_{\theta\theta}) + \beta v. \quad (2.100)$$

Derivation. Since the LHS is of order $O(\varepsilon)$, the $O(1)$ phase field equation is not affected by the inclusion of this term. However in the next order we will have one extra term in

the equation. The solvability condition is then slightly different. Basically, the term H of equation (2.97) must be replaced by

$$H := \varepsilon \alpha v \frac{\partial \Phi^0}{\partial z} + \sum_{m=1}^M \varepsilon \left(-\kappa \bar{\chi}_{B^m} \frac{\partial^{2m-1}}{\partial z^{2m-1}} + \varepsilon^{2m} \bar{\chi}_{C^m} \frac{\partial^{2m}}{\partial z^{2m-1} \partial s} \right) \Phi^0 + \varepsilon G'(\Phi^0)u \quad (2.101)$$

and L is defined as before. Since $d\Phi^0/d\rho$ solves $L\Psi = 0$, by the Fredholm theorem

$$\left(L\hat{\Phi}^1, \frac{\partial}{\partial z}\Phi^0 \right) = \left(H, \frac{\partial}{\partial z}\Phi^0 \right) = 0$$

Hence, we conclude that

$$-u[s]_E = \kappa(\sigma + \sigma_{\theta\theta}) + \|\partial\Phi^0/\partial z\|^2 v,$$

i.e., for $\beta := \|\partial\Phi^0/\partial z\|^2$, one has the result (5.42).

2.4.4 A Numerical Example

To see possible applications we consider a system in $2-d$ which interacts through a toy potential that consists of two parts. One part is isotropic and short range, the other anisotropic and longer range, i.e.,

$$\begin{aligned} J(r, \theta) &= J_1(r) + \delta J_2(r) \cos 6\theta \\ J_1(r) &= \frac{\exp(-r^2)}{\pi}, \quad J_2(r) = \frac{r^2 \exp(-r^2)}{\pi} \end{aligned} \quad (2.102)$$

To zeroth order, this yields a differential equation of the form

$$\begin{aligned} 0 &= b_6 \Phi^{(6)} + b_4 \Phi^{(4)} + b_2 \Phi^{(2)} + W'(\Phi) \\ \Phi(\pm 5) &= \pm 1, \quad \Phi^{(1)}(\pm 5) = 0, \quad \Phi^{(2)}(\pm 5) = 0 \end{aligned} \quad (2.103)$$

where $b_2 = \frac{1}{4}$, $b_4 = \frac{1}{32}$, $b_6 = \frac{1}{384}(1 + \frac{d \cos 6\theta}{5})$ and $W'(\Phi) = \Phi - \Phi^3$. To solve the above high order non linear differential equation we use finite difference scheme. We discretize the interval

$[-5, 5]$ into K equal pieces and enumerate the points $x_0 = -5, \dots, x_{K+1} = 5$. while second, fourth and sixth order derivatives are numerically approximated by

$$\begin{aligned}\frac{d^2\Phi(x_i)}{dx^2} &\cong \frac{\Phi(x_{i+1}) - 2\Phi(x_i) + \Phi(x_{i-1}))}{\Delta x^2}, \\ \frac{d^4\Phi(x_i)}{dx^4} &\cong \frac{\Phi(x_{i+2}) - 4\Phi(x_{i+1}) + 6\Phi(x_i) - 4\Phi(x_{i-1}) + \Phi(x_{i-2}))}{\Delta x^2}, \\ \frac{d^6\Phi(x_i)}{dx^6} &\cong \frac{\Phi(x_{i+3}) - 6\Phi(x_{i+2}) + 15\Phi(x_{i+1}) - 20\Phi(x_i) + 15\Phi(x_{i-1}) - 6\Phi(x_{i-2}) + \Phi(x_{i-3}))}{\Delta x^6}\end{aligned}\tag{2.104}$$

respectively. Then, the discrete system constitutes a non-linear algebraic equations with $K + 1$ unknowns.

This algebraic equation is solved using a multi-dimensional version of Newton's method. For mesh sizes $\Delta x < \frac{1}{40}$ the value of the surface tension does not change appreciably, but the matrices constructed in the scheme become close to singular when $\Delta x < \frac{1}{80}$. So we take $\Delta x = 1/60$ in our calculations. The phase profile obtained is shown in 2.

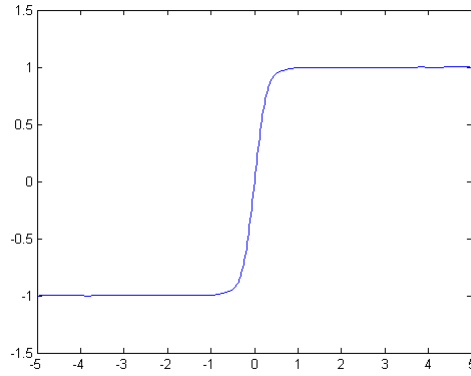


Figure 2: The phase profile

As the solution will change for changing values of θ , the calculated surface tension will change too accordingly by the formula

$$\sigma = \sum_{i=0}^{i=K} \left(W(\Phi(x_i)) - \frac{W'(\Phi(x_i))\Phi(x_i)}{2} \right) \Delta x \tag{2.105}$$

The surface tension is calculated as $\sigma(0) = 0.321$ and $\sigma(\pi/6) = 0.314$, hence the anisotropy of the surface tension is $\frac{\gamma_{\max} - \gamma_{\min}}{\gamma_{\text{avg}}} \cong 2\%$. The $\sigma - plot$ is shown 3

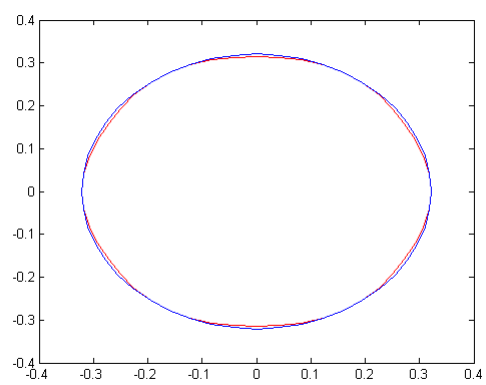


Figure 3: The polar plot

3.0 INTEGRAL PHASE FIELD EQUATIONS

In the previous chapter we have seen the importance of the correlation terms in the free energy. We tried to remedy the situation by introducing higher order derivative terms. The approach allowed us to calculate the surface tension without ignoring the microscopic effects and verify the interfacial conditions. However, there were two main obstacles in front of the method to make it a practical tool for realistic calculations. First of all the formulation of the method was done in two dimensions. Secondly, it required one to solve higher order non-linear differential equations.

In this chapter we generalize the results of the previous one to arbitrary dimensions. However this is not immediate, as the polar coordinate approach is inadequate. Beyond the geometric issues, it is also desirable to seek a formulation in which one retains all of the detailed anisotropy. We resolve these problems by presenting results on a general set of interactions that contain both local and non-local interactions in arbitrary dimension. Instead of approximating Ising type interactions with mean field and solving the corresponding phase field equation, a direct integral equation form is formulated, accomplishing the following objectives simultaneously:

- i)* The formulation is physically exact (as a continuum model);
- ii)* The formulation is valid for an arbitrary dimension;
- iii)* The existence of solutions to the integral equations is easily established using the current theory [80];
- iv)* There is an asymptotically stable numerical scheme for the solutions of the integral equations.

3.1 ANISOTROPIC INTERFACE RELATIONS WITH NON-LOCAL INTERACTIONS

In this section we present the idea of working directly on the integral form (see also [73]) with both local and non-local interactions. This has a number of advantages, as summarized above, particularly in terms of avoiding arbitrarily large order differential equations.

We shall use a phase field model from a free energy functional comprising a linear combination of a local interaction term $\int a(\vec{\nabla}\phi(x)dx$ and a non-local interaction term $\int \int J_\varepsilon(x-y)[\phi(x) - \phi(y)]^2 dx dy$.

For the physical motivation, we consider a microscopic lattice system involving a set of “spins”, denoted by a real value ϕ_k for each lattice point k , and interactions of strength J_{kl} between these spins. In statistical mechanics, the (reduced) Hamiltonian of this physical system is described by

$$H_{interaction}[\phi] = \sum_{k,l} \frac{1}{4} (\phi_k - \phi_l)^2 J_{kl}.$$

The entropic part of the free energy which is the temperature times the logarithm of the number of accessible states times $\{\sim \phi_k \ln \phi_k + (1 - \phi_k) \ln(1 - \phi_k)\}$ is often approximated in applications by a smooth double well potential, denoted $W(\phi_k)$, which takes its minimum values on the bulk (i.e., single phase) material. In particular, $\phi_k \simeq 1$ denotes the higher energy phase (liquid), while $\phi_k \simeq -1$ denotes the lower energy (solid). Moreover, in under-cooled melts, the free energy is further reduced by an amount proportional to latent heat. These ideas lead to the free energy that can be written as

$$F[\phi] = \sum_{k,l} \frac{1}{4} J_{kl} (\phi_k - \phi_l)^2 + \sum_k W(\phi_k) + \sum_k (T - T_E) G(\phi_k). \quad (3.1)$$

When passing to the continuum limit, the interaction strength must be scaled appropriately [20]. In the continuum limit we replace the summation by integrals (and the physical quantities by their calligraphic counterparts). Adding a local interaction term to the Hamiltonian and writing everything in dimensionless units, we arrive at the functional form of the

interfacial excess free energy:

$$\begin{aligned} \mathcal{F}[\phi] = & \frac{\lambda}{2} \int a(\vec{\nabla} \phi(x)) dx + \frac{(1-\lambda)}{4} \int J_\varepsilon(x-y)(\phi(x) - \phi(y))^2 dx dy \\ & + \int W(\phi(x)) dx + \int (T - T_E) S(\phi(x)) dx \end{aligned} \quad (3.2)$$

where $J_\varepsilon(z) = \varepsilon^{-N} J(\varepsilon^{-1}z)$ and ε is an atomic length scale. For simplicity we assume $\Omega = \mathbb{R}^N$ with $N \geq 2$. The following conditions are imposed: $\lambda \in [0, 1]$ is a constant and $a(\zeta) = \zeta A \zeta^T$ where $A = (A)_{ij}$ is a semi-positive definite constant matrix. Since the energy does not change when $J_\varepsilon(x)$ is replaced by $\frac{1}{2}[J_\varepsilon(x) + J_\varepsilon(-x)]$, J_ε can be assumed to be even. Also, for simplicity, we take $\Omega = \mathbb{R}^N$ ($N \geq 2$). We make the following assumptions:

1. $\lambda \in [0, 1]$ is a constant and $a(\zeta) = \zeta A \zeta^T$ where A is a semi-positive definite constant matrix;
2. $J_\varepsilon(x) = \varepsilon^{-N} J(\varepsilon^{-1}x)$ where $J \in C^1(\mathbb{R}^N)$ satisfies
$$J(x) = J(-x) \geq 0 \quad \forall x \in \mathbb{R}^N, \quad \int_{\mathbb{R}^N} J(x) dx = 1, \quad \int_{\mathbb{R}^N} |x|^3 J(x) dx < \infty.$$
3. $W \in C^\infty([-1, 1])$, $0 = W(\pm 1) < W(\phi) \forall \phi \neq \pm 1$, $W''(\pm 1) > 0$;
4. Either λA is positive definite or $W''(\phi) > \lambda - 1 \quad \forall \phi \in [-1, 1]$;
5. $G \in C^2([-1, 1])$, $G(1) - G(-1) = 1$, $G'(\pm 1) = 0$.

The phase field equation for the order parameter is a gradient flow for the free energy. For a smooth ψ with compact support we can calculate the first variation of \mathcal{F} in the direction ψ by

$$\begin{aligned} \left\langle \frac{\delta \mathcal{F}[\phi]}{\delta \phi}, \psi \right\rangle & : = \lim_{\delta \rightarrow 0} \frac{\mathcal{F}[\phi + \delta \psi] - \mathcal{F}[\phi]}{\delta} \\ & = \int_{\mathbb{R}^N} \psi \left\{ -\varepsilon \lambda A : D^2 \phi + \frac{W'(\phi)}{\varepsilon} - u G'(\phi) - \frac{1-\lambda}{\varepsilon} [J_\varepsilon * \phi - \phi] \right\} dx \end{aligned}$$

where

$$J_\varepsilon * \phi(x) := \int_{\mathbb{R}^N} J_\varepsilon(x-y) \phi(y) dy = \int_{\mathbb{R}^N} J(y) \phi(x - \varepsilon y) dy.$$

Here $D^2 \phi = (\phi_{x^i x^j})_{N \times N}$ and for $N \times N$ matrices $C = (c^{ij})_{N \times N}$ and $D = (d_{ij})_{N \times N}$,

$$C : D = \sum_{i,j=1}^N c^{ij} d_{ij} = \text{Trace}(C^T D), \quad A : D^2 \phi = \sum_{i,j=1}^N a^{ij} \phi_{x^i x^j}.$$

The phase field equation is taken as φ_t being proportional to $-\delta\mathcal{F}/\delta\phi$, i.e.,

$$\varepsilon^2\tau\varphi_t = \varepsilon^2\lambda A : D^2\varphi + (1 - \lambda)(J_\varepsilon * \varphi - \varphi) - W'(\varphi) + \varepsilon u G'(\varphi) \quad (3.3)$$

where $\tau > 0$ is a scaled relaxation time. We are interested in the asymptotic behavior of the solution as $\varepsilon \searrow 0$, with fixed λ, τ and A . When necessary, we shall write the solution of (3.3) as $\varphi = \varphi_\varepsilon(x, t)$.

Remark 9. Traditionally [24], G is taken as $G(\varphi) = \varphi/2$. Here the assumption $G'(\pm 1) = 0$ provides a number of advantages over the traditional one. The condition $G'(\pm 1) = 0$ implies that both $\varphi \equiv 1$ and $\varphi \equiv -1$ are solutions of (3.3), so it ensures that any physical relevant solution of (3.3) satisfies $|\varphi| \leq 1$. In addition, in a matched asymptotic expansion, the outer expansion is trivial: $\varphi^{\text{outer}} \equiv 1$ in the liquid region and $\varphi^{\text{outer}} \equiv -1$ in the solid region.

In the sequel, we regard $x = (x^1, \dots, x^N)^T$ as a column vector and $\nabla\phi = (\phi_{x_1}, \dots, \phi_{x_N})$ as a row operator. Also, for vectors $c = (c_i)_{N \times 1}$ (or $(c_i)_{1 \times N}$) and $d = (d_i)_{N \times 1}$ (or $(d_j)_{1 \times N}$), we denote

$$c \otimes d = (c_i d_j)_{N \times N}, \quad A : \nabla\phi \otimes \nabla\phi = \nabla\phi A \nabla^T \phi = \sum_{i,j=1}^N \phi_{x_i} a^{ij} \phi_{x_j} = a(\nabla\phi).$$

Using convolution, we can write the free energy as

$$\mathcal{F}[\phi] = \int_{\mathbb{R}^N} \left\{ \frac{\lambda\varepsilon}{2} A : \nabla\phi \otimes \nabla\phi + \frac{1-\lambda}{2\varepsilon} \phi[\phi - J_\varepsilon\phi] + \frac{W(\phi)}{\varepsilon} - uG(\phi) \right\} dx. \quad (3.4)$$

3.2 PLANAR INTERFACE AND SURFACE TENSION

In this section, we seek solutions of (3.3) that represent stationary planar interfaces at the melting temperature. For this purpose, we assume that $u \equiv 0$.

3.2.1 Stationary Solution with Planar Interfaces.

Given a point $x_0 \in \mathbb{R}^N$ and a direction $\zeta \in \mathbb{R}^N \setminus \{0\}$, we seek a stationary solution of (3.3) such that $\varphi(x_0, t) = 0$ and all level sets of φ are hyperplanes perpendicular to ζ ; this is equivalent to seek a solution of the form

$$\varphi(x, t) = Q(\zeta, z), \quad z := \frac{(x - x_0) \cdot \zeta}{\varepsilon} \in \mathbb{R}. \quad (3.5)$$

Under this special form, we can calculate

$$\varepsilon^2 A : D^2 \varphi(x, t) = a(\zeta) Q_{zz}(\zeta, z), \quad a(\zeta) := A : \zeta \otimes \zeta = \zeta^T A \zeta = |\sqrt{A} \zeta|^2.$$

Making the change of variables $y = \hat{z}\zeta + y'$ with $\hat{z} \in \mathbb{R}$ and $y' \perp \zeta$, we obtain $dy = |\zeta| d\hat{z} dy'$ so that

$$\begin{aligned} J_\varepsilon * \varphi(x, t) &= \int_{\mathbb{R}^N} J(y) \varphi(x - \varepsilon y, t) dy = \int_{\mathbb{R}^N} J(y) Q(\zeta, z - y \cdot \zeta) dy \\ &= \int_{\mathbb{R}} Q(\zeta, z - \hat{z}) |\zeta| \int_{y' \perp \zeta} J(\hat{z}\zeta + y') dy' d\hat{z} = j(\zeta) * Q(\zeta) \end{aligned} \quad (3.6)$$

where $j(\zeta) = j(\zeta, \cdot)$ is defined by

$$j(\zeta, z) := |\zeta| \int_{y' \perp \zeta} J(z\zeta + y') dy' \quad \forall z \in \mathbb{R}. \quad (3.7)$$

Thus, for certain boundary conditions of interest, $u \equiv 0$, $\varphi(x, t) = Q(\zeta, (x - x_0) \cdot \zeta / \varepsilon)$ is a stationary solution of (3.3) if $Q(\zeta)$ solves the following boundary value problem of an autonomous integral-differential equation

$$\begin{cases} \lambda a(\zeta) Q_{zz} + (1 - \lambda)[j(\zeta) * Q - Q] - W'(Q) = 0 & \mathbb{R}, \\ \lim_{z \rightarrow \pm\infty} Q(\zeta, z) = \pm 1, \quad Q(\zeta, 0) = 0. \end{cases} \quad (3.8)$$

For fixed $\zeta \in \mathbb{R}^N \setminus \{0\}$, it is easy to verify that

$$j(\zeta, z) = j(\zeta, -z) = j(-\zeta, z) \geq 0 \quad \forall z \in \mathbb{R}, \quad \int_{\mathbb{R}} j(\zeta, z) dz = 1, \quad \int_{\mathbb{R}} |z|^3 j(\zeta, z) dz < \infty.$$

Also, when λA is positive definite, $\lambda a(\zeta) > 0$; when λA is not positive definite, $\lambda a(\zeta) \geq 0$ but in this case we have assumed that the function $\phi \in [-1, 1] \rightarrow (1 - \lambda)\phi + W'(\phi)$ is increasing. Hence, from a general theory of Chen [80], we have the following:

Lemma 10. *For each $\zeta \in \mathbb{R}^{N-1} \setminus \{0\}$, problem (3.8) admits a unique solution. In addition, the solution is smooth, strictly monotonic, and globally asymptotically stable for the 1-D dynamics*

$$\begin{cases} \varphi_t = \lambda a(\zeta) \varphi_{zz} + (1 - \lambda)[j(\zeta) * \varphi - \varphi] - W'(\varphi) & \mathbb{R} \times (0, \infty), \\ \varphi(\cdot, 0) = \varphi_0(\cdot) & \mathbb{R} \times \{0\}. \end{cases}$$

Here “globally asymptotically stable” means that there exist constants $c \in (0, 1)$ and $\nu > 0$ such that if $\|\varphi_0\|_{L^\infty(\mathbb{R})} \leq 1$, $\underline{\lim}_{z \rightarrow \infty} \varphi_0(z) \geq c$, and $\overline{\lim}_{z \rightarrow -\infty} \varphi_0(z) \leq -c$, then for some $z_0 \in \mathbb{R}$ and $K > 0$,

$$\|\varphi(\cdot, t) - Q(\zeta, \cdot - z_0)\|_{L^\infty(\mathbb{R})} \leq K e^{-\nu t} \quad \forall t > 0.$$

3.2.2 Interfacial Energy Density

Notice that when $u \equiv 0$ and $\phi(x) = Q(\zeta, (x - x_0) \cdot \zeta / \varepsilon)$, the integrand in (3.2) is a positive constant on each hyperplane that is perpendicular to ζ , so the integral is unbounded. A relevant quantity is the integral along any line in the direction ζ , say, $\zeta\mathbb{R} := \{z\zeta \mid z \in \mathbb{R}\}$. Hence, we define

$$\sigma(\zeta) := \int_{\mathbb{R}} \left\{ \frac{\lambda a(\zeta)}{2} Q_z^2 + W(Q) + \frac{1 - \lambda}{2} Q(Q - j(\zeta) * Q) \right\} dz \big|_{Q=Q(\zeta, \cdot)}. \quad (3.9)$$

Clearly, $\sigma(\zeta)$ does not depend on ε and x_0 . When $\zeta = \mathbf{n}$ is a unit vector, we call $\sigma(\mathbf{n})$ the **interfacial energy density** for interfaces with unit normal \mathbf{n} . If γ is a macroscopically observed solid-liquid interface, its total interfacial energy is defined as

$$\int_{\gamma} \sigma(\mathbf{n}(x)) H^{N-1}(dx)$$

where $\mathbf{n}(x)$ is the unit normal of γ at $x \in \gamma$ (pointing from solid to liquid), and $H^{N-1}(dx)$ is the surface element of γ . We call $\sigma : \mathbb{R}^{N-1} \setminus \{0\} \rightarrow (0, \infty)$ the naturally extended interfacial energy density, or simply the interfacial energy density function.

Remark 11. Since $j(\zeta, \cdot)$ is an even function, $Q(\zeta, \cdot)$ is an odd function and numerically it can be obtained by taking the limit, as $t \rightarrow \infty$, of a solution of (3.8) with odd initial data that approaches 1 as $z \rightarrow \infty$. For example, one can choose a small positive Δt and perform the following:

$$\phi_0(z) = \tanh z \quad \forall z \in \mathbb{R}^n, \quad (3.10)$$

$$\phi_{k+1} = \phi_k + \Delta t \{ \lambda a(\zeta) \phi_k'' + (1 - \lambda) [j(\zeta) * \phi_k - \phi_k] - W'(\phi_k) \},$$

$$Q(\zeta) = \lim_{k \rightarrow \infty} \phi_k,$$

$$\sigma(\zeta) = \int_{\mathbb{R}} \left(W(Q) - \frac{1}{2} Q W'(Q) \right) dz \big|_{Q=Q(\zeta)}. \quad (3.11)$$

Here the formula (3.11) is obtained from (3.9) by an integration by parts and a substitution of the integro-differential equation for $Q(\zeta)$.

In the sequel, $Q_\zeta = (Q_{\zeta^1}, \dots, Q_{\zeta^N})$ is the gradient of $Q(\zeta, z)$ with respect to ζ . Also $D^2\sigma = (\sigma_{\zeta^k \zeta^l})_{N \times N}$ is the Hessian of $\sigma(\zeta)$. The following will be used later in deriving interfacial conditions for solutions of the phase field equation (3.3).

Lemma 12. The interfacial energy density function σ has the following properties:

1. σ is even and homogeneous of degree one, i.e.

$$\sigma(L\mathbf{n}) = |L|\sigma(\mathbf{n}) \quad \forall L \neq 0, \mathbf{n} \in \mathbb{S}^{N-1};$$

Consequently,

$$\zeta \cdot \nabla \sigma(\zeta) = \sigma(\zeta), \quad D^2\sigma(\zeta) \zeta = (0)_{N \times 1}, \quad \zeta^T D^2\sigma(\zeta) = (0)_{1 \times N}. \quad (3.12)$$

2. Using the abbreviation Q for $Q(\zeta, z)$ and \hat{Q} for $Q(\zeta, z - y \cdot \zeta)$, we have

$$D^2\sigma(\zeta) = \int_{\mathbb{R}} Q_z \left(\lambda [A Q_z + 2A\zeta \otimes Q_\zeta] + (1 - \lambda) \int_{\mathbb{R}^N} J(y) \left(\frac{y \otimes y}{2} \hat{Q}_z - y \otimes \hat{Q}_\zeta \right) dy \right) dz.$$

Proof. (1) Since $j(\zeta, z)$ is even in z and in ζ and the solution of (3.8) is unique, it is easy to verify that $Q(-\zeta, z) = Q(\zeta, -z)$, so by (3.11), $\sigma(\zeta) = \sigma(-\zeta)$. Similarly, for $\mathbf{n} \in \mathbb{S}^{N-1}$ and $\zeta = L\mathbf{n}$ with $L > 0$, both $Q(\mathbf{n}, x \cdot \mathbf{n}/\varepsilon)$ and $Q(\zeta, x \cdot \zeta/\varepsilon)$ represent the same stationary solution of (3.3) with planar interfaces perpendicular to \mathbf{n} , so one can verify that $Q(\zeta, z) = Q(\mathbf{n}, z/L)$. It then follow from (3.11) that $\sigma(\zeta) = L\sigma(\mathbf{n})$. Thus, $\sigma(\cdot)$ is even and homogeneous of degree one.

Now differentiating $t\sigma(\zeta) = \sigma(t\zeta)$ with respect to t and setting $t = 1$ we have $\sigma(\zeta) = \zeta \cdot \nabla \sigma(\zeta)$. Differentiating this relation with respect to ζ^k we obtain $\sigma_{\zeta^k} = \sigma_{\zeta^k} + \zeta \cdot \nabla \sigma_{\zeta^k}$ so $\zeta \cdot \nabla \sigma_{\zeta^k} = 0$. This implies that $\zeta^T D^2 \sigma(\zeta) = \mathbf{0}$, $D^2 \sigma(\zeta) \zeta = \mathbf{0}$.

(2) Using the abbreviation Q for $Q(\zeta, z)$ and \hat{Q} for $Q(\zeta, z - y \cdot \zeta)$ we can write (3.9) as

$$\sigma(\zeta) = \int_{\mathbb{R}} \frac{\lambda a(\zeta)}{2} Q_z^2 + W(Q) + \frac{1-\lambda}{2} Q \int_{\mathbb{R}^N} J(y)[Q - \hat{Q}] dy dz. \quad (3.13)$$

Since $j(\zeta, \cdot)$ is an even function, denoting by $\langle \cdot, \cdot \rangle$ the $L^2(\mathbb{R})$ inner product, we have

$$\langle f, j(\zeta) * g \rangle = \int_{\mathbb{R}} \int_{\mathbb{R}} f(z) j(\zeta, z - \hat{z}) g(\hat{z}) dz d\hat{z} = \langle j(\zeta) * f, g \rangle.$$

Differentiating (3.13) with respect to ζ^k and using the above identity with $f = Q$ and $g = Q_{\zeta^k}$ we then obtain,

$$\begin{aligned} \frac{\partial \sigma(\zeta)}{\partial \zeta^k} &= \int_{\mathbb{R}} \lambda a(\zeta) Q_z Q_{z\zeta^k} dz + W'(Q) Q_{\zeta^k} + (1-\lambda) Q_{\zeta^k} [Q - j(\zeta) * Q] dz \\ &\quad + \int_{\mathbb{R}} \frac{\lambda a_{\zeta^k}(\zeta)}{2} Q_z^2 dz + \frac{1-\lambda}{2} Q \int_{\mathbb{R}^N} J(y) y^k Q_z(\zeta, z - y \cdot \zeta) dy dz. \end{aligned}$$

Note that $a_{\zeta^k}(\zeta) = 2 \sum_{i=1}^N a^{ki} \zeta_i =: 2(A\zeta)^k$. Also, the first integral equals, by integration by parts,

$$\int_{\mathbb{R}} Q_{\zeta^k} (-\lambda a(\zeta) Q_{zz} + W'(Q) - (1-\lambda)[j(\zeta) * Q - Q]) dz = 0$$

by the integral-differential equation for $Q = Q(\zeta, z)$. Thus,

$$\frac{\partial \sigma(\zeta)}{\partial \zeta^k} = \int_{\mathbb{R}} \lambda (A\zeta)^k Q_z^2 dz + \frac{1-\lambda}{2} Q \int_{\mathbb{R}^N} J(y) y^k Q_z(\zeta, z - y \cdot \zeta) dy dz.$$

Consequently, one more differentiation gives

$$\begin{aligned} \frac{\partial^2 \sigma(\zeta)}{\partial \zeta^k \partial \zeta^l} &= \int_{\mathbb{R}} \{ \lambda a^{kl} Q_z^2 + 2\lambda (A\zeta)^k Q_z Q_{\zeta^l} \} dz + \frac{1-\lambda}{2} \int_{\mathbb{R}} Q_{\zeta^l} \int_{\mathbb{R}^N} J(y) y^k \hat{Q}_z dy dz \\ &\quad + \frac{1-\lambda}{2} \int_{\mathbb{R}} Q \int_{\mathbb{R}^N} J(y) y^k [\hat{Q}_{z\zeta^l} - y^l \hat{Q}_{zz}] dy dz. \end{aligned}$$

Since $y^k J(y)$ is an odd function, we have

$$\int_{\mathbb{R}} Q_{\zeta^l} \int_{\mathbb{R}^N} J(y) y^k \hat{Q}_z dy dz = - \int_{\mathbb{R}} Q_z \int_{\mathbb{R}^N} J(y) y^k \hat{Q}_{\zeta^l} dy dz.$$

Also, integration by parts in z we have

$$\int_{\mathbb{R}} Q \int_{\mathbb{R}^N} J(y) y^k [\hat{Q}_{z\zeta^l} - y^l \hat{Q}_{zz}] dy dz = - \int_{\mathbb{R}} Q_z \int_{\mathbb{R}^N} J(y) y^k [\hat{Q}_{\zeta^l} - y^l \hat{Q}_z] dy dz.$$

Substituting the last two identities into the expression of $\sigma_{\zeta^k \zeta^l}$ we then obtain the second assertion of the Lemma. This completes the proof. \square

3.2.3 A Solvability Condition

For $\zeta \in \mathbb{R}^N \setminus \{0\}$, consider the linear operator \mathcal{L}^ζ defined by

$$\mathcal{L}^\zeta \phi = \lambda a(\zeta) \phi_{zz} + (1-\lambda)[j(\zeta) * \phi - \phi] - W''(Q(\zeta))\phi.$$

Lemma 13. *Let $\zeta \in \mathbb{R}^N \setminus \{0\}$ and $Q = Q(\zeta, \cdot)$. Then*

$$\mathcal{L}^\zeta Q_z \equiv 0, \quad \mathcal{L}^\zeta Q_\zeta = -2\lambda(A\zeta)Q_{zz} + (1-\lambda) \int_{\mathbb{R}^N} J(y) y Q_z(\zeta, z - y \cdot \zeta) dy. \quad (3.14)$$

In addition, for every $m \in \mathbb{R}$ and bounded f satisfying $f(\pm\infty) = 0$, the equation

$$\mathcal{L}^\zeta \phi = f \text{ on } \mathbb{R}, \quad \phi(\pm\infty) = 0, \quad \phi(0) = m$$

has a unique solution if and only if

$$\int_{\mathbb{R}} Q_z(\zeta, z) f(z) dz = 0. \quad (3.15)$$

Proof. (1) The first assertion follows by differentiating (3.8) with respect to z and ζ and using $a(\zeta)_\zeta = 2A\zeta$ and

$$\frac{\partial}{\partial \zeta} j(\zeta) * Q = \frac{\partial}{\partial \zeta} \int_{\mathbb{R}^N} J(y) Q(\zeta, z - y \cdot \zeta) dy = j * Q_\zeta - \int_{\mathbb{R}^N} J(y) y Q_z(\zeta, z - y \cdot \zeta) dy.$$

(2) Since $j(\zeta, \cdot)$ is even, one can check that \mathcal{L}^ζ is self-adjoint in the sense that

$$\langle \mathcal{L}^\zeta \phi, \psi \rangle = \langle \phi, \mathcal{L}^\zeta \psi \rangle \quad \forall \phi, \psi \in C_0^\infty(\mathbb{R}).$$

Also, 0 is an eigenvalue of \mathcal{L}^ζ with eigenvector $Q_z(\zeta, \cdot)$. Since $W''(\pm 1) > 0$ and $Q_z(\zeta, \cdot) > 0$ on \mathbb{R} , one can show that 0 is a simple eigenvalue and the remaining spectrum of \mathcal{L}^ζ lies on the half-plane $\{\mu \in \mathbb{C} \mid \operatorname{Re}(\mu) < -\mu_0\}$ for some positive real number $\mu_0 \leq \min\{W''(1), W''(-1)\}$. The assertion then follows from the Fredholm alternative, for which we omit further technical details. When (3.15) holds, there are infinitely many solutions, each of which can be written as $\phi(z) = \phi_{\text{sp}}(z) + cQ_z(\zeta, z)$ where c is an arbitrary constant and ϕ_{sp} is a special solution. Since $Q_z(\zeta, 0) > 0$, when the extra condition $\phi(0) = m$ is imposed, the constant c is uniquely determined so the solution is unique. \square

3.3 SOME DIFFERENTIAL GEOMETRY

In studying free boundary problems, quite often one needs local representations of free boundaries. Here we briefly present a key technique used in formal asymptotic expansions from a differential geometry perspective.

3.3.1 Local Coordinates

Let $\Gamma = \cup_{0 \leq t \leq T} (\Gamma_t \times \{t\}) \subset \mathbb{R}^N \times [0, T]$ be a smooth N -dimensional manifold, where $[0, T]$ is time interval of interest. Fixing an arbitrary point on Γ , we can parameterize Γ near that point by a local chart, denoted by

$$X_0(s', t) \in \Gamma_t, \quad s' = (s^1, \dots, s^{N-1}) \in \mathbb{R}^{N-1}.$$

Fixing an orientation, we denote by $\mathbf{n}(s', t)$ the unit normal of Γ_t at $X_0(s', t)$ and define

$$X(s, t) := X_0(s', t) + s^N \mathbf{n}(s', t), \quad s = (s', s^N) = (s^1, \dots, s^N) \in \mathbb{R}^N.$$

Then locally $x = X(s, t)$ is a diffeomorphism. We denote by $s = S(x, t) = (S'(x, t), S^N(x, t))$ the inverse of $x = X(s, t)$ so that

$$x = X_0(S'(x, t), t) + S^N(x, t) \mathbf{n}(S'(x, t), t). \quad (3.16)$$

3.3.2 Curvature and Normal Velocity

(1) It is easy to see that $h(x, t) := S^N(x, t)$ is the signed distance from x to Γ_t . In addition differentiating the identity (3.16) with respect to x we have

$$\delta^{ij} = \frac{\partial x^i}{\partial x^j} = \frac{\partial X^i(S(x, t), t)}{\partial x^j} = \sum_{k=1}^{N-1} (X_{0s^k}^i + s^N \mathbf{n}_{s^k}^i) S_{x^j}^k + \mathbf{n}^i S_{x^j}^N.$$

Thus,

$$\mathbf{n}^j = \sum_{i=1}^N \mathbf{n}^i \delta^{ij} = \sum_{k=1}^{N-1} (\mathbf{n} \cdot X_{0s^k} + s^N \mathbf{n} \cdot \mathbf{n}_{s^k}) S_{x^j}^k + \mathbf{n} \cdot \mathbf{n} S_{x^j}^N = S_{x^j}^N.$$

Here we have used the fact that X_{0s^k} is a tangent vector of Γ_t , so it is perpendicular to \mathbf{n} . Hence,

$$\nabla S^N(x, t) = \mathbf{n}(s', t).$$

This equation explains that the normal \mathbf{n} of the interface, originally defined on Γ_t , can be extended to a neighborhood of Γ_t (by constant along normal lines), so that

$$\nabla \mathbf{n} := \nabla \mathbf{n}(S'(x, t), t) = D^2 S^N(x, t).$$

It is easy to see that \mathbf{n} is an eigenvector of $\nabla \mathbf{n}$ with eigenvalue zero. Let $\{\mathbf{n}, \tau_1, \dots, \tau_{N-1}\}$ be an orthonormal eigenbasis of $\nabla \mathbf{n}$ with corresponding eigenvalues $\{0, \kappa^1, \dots, \kappa^{N-1}\}$. Restricting x to the point $X_0(s', t)$, the eigenvalues $\{\kappa^1, \dots, \kappa^{N-1}\}$ are called **principal curvatures** of Γ_t at $X_0(s', t)$, and $\{\tau_1, \dots, \tau_{N-1}\}$ the corresponding **principal directions**. It then follows by the decomposition of a symmetric matrix that

$$\nabla \mathbf{n}(S'(x, t), t) |_{x=X_0(s', t)} = D^2 S^N(X_0(s', t), t) = \sum_{i=1}^{N-1} \kappa^i \tau_i \otimes \tau_i. \quad (3.17)$$

(2) Next differentiating (3.16) with respect to t gives

$$\mathbf{0} = \frac{\partial x}{\partial t} = X_{0t} + \sum_{k=1}^{N-1} (X_{0s^k} + s^N \mathbf{n}_{s^k}) S_t^k + \mathbf{n} S_t^N + S^N \mathbf{n}_t.$$

Taking the inner product with \mathbf{n} we obtain $0 = X_{0t} \cdot \mathbf{n} + S_t^N$ so that

$$S_t^N(x, t) = -X_{0t}(s', t) \cdot \mathbf{n}(s', t) = -v(X_0(s', t), t)$$

where $v(X_0(s', t), t) := X_{0t}(s', t) \cdot \mathbf{n}(s', t)$ is called the **normal velocity** of Γ_t at $X_0(s', t)$ in the normal direction $\mathbf{n}(s', t)$. Here again, $S_t^N(x, t)$ is constant along the normal lines.

3.3.3 The Stretched Variable

Let $\varphi = \varphi_\varepsilon$ be a solution of (3.3) and $\Gamma_t^\varepsilon := \{x \mid \varphi_\varepsilon(x, t) = 0\}$ be the zero level set of φ_ε . With respect to the ε -independent reference manifold Γ_t , we represent Γ_t^ε locally as

$$X_\varepsilon(s', t) := X_0(s', t) + \varepsilon H_\varepsilon(s', t) \mathbf{n}(s', t) \in \Gamma_t^\varepsilon,$$

where $\varepsilon H_\varepsilon$ admits an expansion $\varepsilon H_\varepsilon(s', t) = \varepsilon h_1(s', t) + \varepsilon^2 h_2(s', t) + \dots$. In this context, h_0 can be regarded as the unknown X_0 . The location of the interface Γ_t^ε is then uniquely determined by the coefficients X_0, h_1, h_2, \dots , of the asymptotic ε power series expansion of X_ε .

We introduce the stretched variable

$$z = Z(x, t) := \frac{S^N(x, t) - \varepsilon H_\varepsilon(S'(x, t), t)}{\varepsilon} = \frac{s^N}{\varepsilon} - H_\varepsilon(s', t).$$

We call (z, s', t) the local coordinates in which Γ_t^ε is represented by $z = 0$.

Remark 14. In the case $u \equiv 0$, the phase field equation (3.3) (with $\lambda = 1$) becomes the well-studied Allen-Cahn equation [18]. It is known that $\varphi_\varepsilon(x, t) = Q(\mathbf{n}_\varepsilon, d_\varepsilon(x, t)/\varepsilon) + O(\varepsilon^2)$ where $d_\varepsilon(x, t)$ is the signed distance from x to the interface Γ_t^ε , with normal \mathbf{n}_ε . This fact leads to a common practice (e.g. [85]) in which $\hat{z} := d_\varepsilon/\varepsilon$ is defined as the stretched variable and the local variables (\hat{s}', \hat{z}, t) are the inverse of

$$\mathbf{x} = X_\varepsilon(\hat{s}', t) + \varepsilon \hat{z} \mathbf{n}_\varepsilon(\hat{s}', t).$$

Comparing with this ε -dependent local chart, our chart $x = X_0(s', t) + \varepsilon[z + H_\varepsilon(s', t)]\mathbf{n}(s', t)$ has advantages and disadvantages. The obvious advantage is that $s' = S'(x, t)$ does not depend on ε . The disadvantage is that $Q(\mathbf{n}(s', t), z)$ is only an $O(\varepsilon)$ approximation of $\varphi_\varepsilon(x, t)$. Using

$$\mathbf{n}_\varepsilon = \mathbf{n} - \varepsilon \nabla H_\varepsilon(S'(x, t), t) + O(\varepsilon^2),$$

$$Q(\mathbf{n}_\varepsilon, z) = Q(\mathbf{n}, z) - \varepsilon \nabla H_\varepsilon(s', t) \cdot Q_\zeta(\mathbf{n}, z) + O(\varepsilon^2),$$

we can eliminate this disadvantage by subtracting the quantity $\varepsilon \nabla H_\varepsilon \cdot Q_\zeta$ from our asymptotic expansion.

3.3.4 Smooth Function Expanded in ε Power Series

The transformation from (z, s', t) to (x, t) can be expressed as

$$x = X_0(s', t) + \varepsilon [z + H_\varepsilon(s', t)] \mathbf{n}(s', t). \quad (3.18)$$

A smooth function $f(x, t)$ for x near Γ_t can be expressed in (z, s', t) via the Taylor expansion

$$f(x, t) = f(X_0, t) + \varepsilon(z + H_\varepsilon)(\mathbf{n} \cdot \nabla)f(X_0, t) + \frac{\varepsilon^2(z + H_\varepsilon)^2}{2}(\mathbf{n} \otimes \mathbf{n} : \nabla \otimes \nabla)f(X_0, t) + \dots$$

where X_0 and H_ε are short for $X_0(s', t)$ and $H_\varepsilon(s', t)$. In particular,

$$\left\{ \begin{array}{l} S_t^N(x, t) = -v(X_0, t), \quad \nabla S^N(x, t) = \mathbf{n}(s', t), \\ S_t^k(x, t) = S_t^k(X_0, t) + \varepsilon[z + H_\varepsilon](\mathbf{n} \cdot \nabla) \nabla S_t^k(X_0, t) + \dots, \\ \nabla S^k(x, t) = \nabla S^k(X_0, t) + \varepsilon[z + H_\varepsilon](\mathbf{n} \cdot \nabla) \nabla S^k(X_0, t) + \dots, \\ D^2 S^k(x, t) = D^2 S^k(X_0, t) + \varepsilon[z + H_\varepsilon](\mathbf{n} \cdot \nabla) D^2 S^k(X_0, t) + \dots. \end{array} \right. \quad (3.19)$$

3.3.5 Chain Rule

As a function of (x, t) , relevant derivatives of Z defined by the second equation in (3.18) are

$$\begin{aligned} Z_t &= \varepsilon^{-1} S_t^N(x, t) - \partial_t H_\varepsilon(S'(x, t), t) = -\varepsilon^{-1} v(X_0, t) - \partial_t H_\varepsilon(s', t), \\ \nabla Z &= \varepsilon^{-1} \mathbf{n}(s', t) - \nabla H_\varepsilon(s', t), \quad D^2 Z = \varepsilon^{-1} \nabla \mathbf{n} - D^2 H_\varepsilon(s', t). \end{aligned}$$

In the sequel, for a function $F(z, s', t)$, we shall use $\tilde{\nabla}$, $\tilde{\partial}_t$, and \tilde{D}^2 to denote the corresponding partial derivatives with respect to t and x , with z considered as a constant:

$$\begin{aligned} \tilde{\nabla} F(z, s', t) &:= \sum_{k=1}^{N-1} F_{s^k}(z, s', t) \nabla S^k(x, t) \big|_{x=X_0(s', t) + \varepsilon[z + H_\varepsilon(s', t)] \mathbf{n}(s', t)}, \\ \tilde{\partial}_t F(z, s', t) &:= \sum_{k=1}^{N-1} F_{s^k}(z, s', t) S_t^k(x, t) \big|_{x=X_0 + \varepsilon[z + H_\varepsilon] \mathbf{n}} + F_t(z, s', t), \\ \tilde{D}^2 F(z, s', t) &= \sum_{k, l=1}^{N-1} F_{s^k s^l} \nabla S^k \otimes \nabla S^l + \sum_{k=1}^{N-1} F_{s^k} D^2 S^k \big|_{x=X_0 + \varepsilon[z + H_\varepsilon] \mathbf{n}}. \end{aligned}$$

Here in the (z, s', t) variable, the expansions in (3.19) are needed for the right-hand side. When $F(z, s', t)$ does not depend on z , the operators $\tilde{\nabla}$, $\tilde{\partial}_t$, \tilde{D}^2 are identical to ∂_t , ∇ , and D^2 , respectively.

Let $F(z, s', t) = f(x, t)$ with x evaluated at $x = X_0(s', t) + \varepsilon[z + H_\varepsilon(s', t)] \mathbf{n}(s', t)$. Then

$$\begin{aligned} f_t(x, t) &= -F_z(z, s', t) [\varepsilon^{-1} v(X_0, t) + \partial_t H_\varepsilon(s', t)] + \tilde{\partial}_t F(z, s', t), \\ \nabla f(x, t) &= \varepsilon^{-1} F_z(z, s', t) \mathbf{n}(s', t) - F_z(z, s', t) \nabla H_\varepsilon(s', t) + \tilde{\nabla} F(z, s', t), \\ D^2 f(x, t) &= \varepsilon^{-2} \mathbf{n} \otimes \mathbf{n} F_{zz} \\ &\quad + \varepsilon^{-1} \left\{ F_z \nabla \mathbf{n} - F_{zz} [\mathbf{n} \otimes \nabla H_\varepsilon + \nabla H_\varepsilon \otimes \mathbf{n}] + [\mathbf{n} \otimes \tilde{\nabla} F_z + \tilde{\nabla} F_z \otimes \mathbf{n}] \right\} \\ &\quad + \tilde{D}^2 F - F_z D^2 H_\varepsilon + F_{zz} \nabla H_\varepsilon \otimes \nabla H_\varepsilon - [\nabla H_\varepsilon \otimes \tilde{\nabla} F_z + \tilde{\nabla} F_z \otimes \nabla H_\varepsilon]. \end{aligned}$$

3.3.6 The Convolution in the Stretched Variable

With $f(x, t) = F(z, s', t)$ where $z = Z(x, t)$ and $s' = S'(x, t)$ we have

$$\begin{aligned} f(x - \varepsilon y, t) &= F(Z(x - \varepsilon y), S'(x - \varepsilon y), t), \\ Z(x - \varepsilon y, t) &= \frac{S^N(x - \varepsilon y, t) - \varepsilon H_\varepsilon(S'(x - \varepsilon y, t), t)}{\varepsilon}. \end{aligned}$$

Using the Taylor's expansion and $\nabla S^N = \mathbf{n}$, $D^2 S^N = \nabla \mathbf{n}$ we derive that

$$Z(x - \varepsilon y, t) = Z(x, t) - y \cdot \mathbf{n}(s', t) + \varepsilon y \cdot \nabla H_\varepsilon + \frac{y \otimes y}{2} : \nabla \mathbf{n} - \frac{\varepsilon^2}{2} y \otimes y : D^2 H_\varepsilon + \dots$$

Here we keep track of only those $O(\varepsilon^2)$ terms that depend on $D^2 H_\varepsilon$. Thus, with $z := Z(x, t)$ and $s' := S'(x, t)$ one has

$$\begin{aligned} f(x - \varepsilon y, t) &= F(z - y \cdot \mathbf{n}, s', t) - \varepsilon y \cdot \tilde{\nabla} F(z - y \cdot \mathbf{n}, s', t) \\ &\quad + F_z(z - y \cdot \mathbf{n}, s', t) \left(\varepsilon y \cdot \nabla H_\varepsilon + \frac{y \otimes y}{2} : \nabla \mathbf{n} - \frac{\varepsilon^2}{2} y \otimes y : D^2 H_\varepsilon \right) + \dots \end{aligned}$$

Hence, abbreviating $F(z - y \cdot \mathbf{n}, s', t)$ as \hat{F} , we have

$$\begin{aligned} J_\varepsilon * f(x, t) &= j(\mathbf{n}) * F + \varepsilon \int_{\mathbb{R}^N} J(y) \left(\left[y \cdot \nabla H_\varepsilon + \frac{y \otimes y}{2} : \nabla \mathbf{n} \right] \hat{F}_z - y \cdot \tilde{\nabla} \hat{F} \right) dy \\ &\quad - \frac{\varepsilon^2 D^2 H_\varepsilon}{2} : \int_{\mathbb{R}^N} y \otimes y \hat{F}_z dy + \dots \end{aligned}$$

3.4 ASYMPTOTIC EXPANSION FOR THE PHASE FIELD EQUATION

Let $\varphi = \varphi_\varepsilon$ be a solution of (3.3) and $\Gamma_t^\varepsilon := \{x \mid \varphi_\varepsilon(x, t) = 0\}$ be the zero level set of φ_ε . Let Γ_t be the limit, as $\varepsilon \searrow 0$, of Γ_t^ε . We call Γ_t the macroscopically observed liquid-solid interface. We would like to derive macroscopically observable interfacial conditions from the microscopic model, i.e., the phase field equation (3.3) for $\varphi = \varphi_\varepsilon(x, t)$.

3.4.1 The Expansion

Using the local coordinates (z, s', t) introduced in the previous section, we write

$$\varphi_\varepsilon(x, t) = \Phi(z, s', t) \quad x = X_0(s', t) + \varepsilon[z + H_\varepsilon(s', t)] \mathbf{n}(s', t).$$

Under the local coordinates (z, s', t) , the differential equation (3.3) can be written as

$$\begin{aligned} 0 = & \lambda a(\mathbf{n}) \Phi_{zz} - W'(\Phi) + (1 - \lambda)[j(\mathbf{n}) * \Phi - \Phi] + \varepsilon \{ \tau v \Phi_z + u G'(\Phi) \} \\ & + \varepsilon \lambda A : \left\{ \Phi_z \nabla \mathbf{n} - 2\Phi_{zz} \mathbf{n} \otimes \nabla H_\varepsilon + 2\mathbf{n} \otimes \tilde{\nabla} \Phi_z \right\} \\ & + \varepsilon (1 - \lambda) \int_{\mathbb{R}^N} J(y) \left(\left[y \cdot \nabla H_\varepsilon + \frac{y \otimes y}{2} : \nabla \mathbf{n} \right] \hat{\Phi}_z - y \cdot \tilde{\nabla} \hat{\Phi} \right) dy \\ & + \varepsilon^2 \left(\tau \Phi_z \partial_t H_\varepsilon - D^2 H_\varepsilon : \left[\lambda A \Phi_z + \frac{1 - \lambda}{2} \int_{\mathbb{R}^N} y \otimes y J(y) \hat{\Phi}_z dy \right] \right) + \dots \end{aligned} \quad (3.20)$$

where $v = v(X_0(s', t), t)$, $u = u(x, t)|_{x=X_0(s', t)+\varepsilon[z+H_\varepsilon(s', t)]}$, $\Phi = \Phi(z, s', t)$, $\hat{\Phi} = \Phi(z - y \cdot \mathbf{n}, s', t)$, and “...” are $O(\varepsilon^2)$ terms that are not relevant to our final conclusion.

We assume the asymptotic expansion

$$\Phi(z, s', t) \sim \Phi_0(z, s', t) + \varepsilon \Phi_1(z, s', t) + \varepsilon^2 \Phi_2(z, s', t) + \dots, \quad (3.21)$$

$$H_\varepsilon(s', t) \sim h_1(s', t) + \varepsilon h_2(s', t) + \varepsilon^2 h_3(s', t) + \dots \quad (3.22)$$

where $\Phi_0, \Phi_1, \Phi_2, \dots, h_1, h_2, \dots$, are smooth functions that do not depend on ε .

The outer expansion yields the simple solutions $\varphi^{\text{outer}}(x) \equiv \pm 1$, so the matching condition becomes $\Phi(\pm\infty, s', t) = \pm 1$. Also, since the zero level set of $\varphi_\varepsilon = \Phi$ is characterized by $z = 0$, we need $\Phi(0, s', t) = 0$. Hence, we impose

$$\Phi_0(\pm\infty, s', t) = \pm 1, \quad \Phi_0(0, s', t) = 0, \quad (3.23)$$

$$\Phi_i(\pm\infty, s', t) = 0, \quad \Phi_i(0, s', t) = 0 \quad \forall i = 1, \dots. \quad (3.24)$$

3.4.2 The Zeroth Order Expansion

Substituting (3.21) into (3.20), expanding both sides in ε powers, and equating the leading order coefficients we obtain the equation

$$\lambda a(\mathbf{n}) \Phi_{0zz} + (1 - \lambda)[j(\mathbf{n}) * \Phi_0 - \Phi_0] - W'(\Phi_0) = 0.$$

With the boundary conditions in (3.23), the solution is uniquely given by

$$\Phi_0(z, s', t) = Q(\mathbf{n}(s', t), z).$$

Note that $\tilde{\nabla}$ is the partial derivative with respect to x with z regarded as a constant. Hence

$$\begin{aligned} \tilde{\nabla} \Phi_0 &= \tilde{\nabla} Q(\mathbf{n}(s', t), z) = \sum_{k=1}^N Q_{\zeta^k}(\mathbf{n}, z) \nabla \mathbf{n}^k(S'(x, t), t) = \sum_{k=1}^N \nabla S_{x_k}^N Q_{\zeta^k} = (\nabla \mathbf{n}) Q_{\zeta}, \\ y \cdot \tilde{\nabla} \Phi_0 &= \nabla \mathbf{n} : y \otimes Q_{\zeta}, \quad A : \mathbf{n} \otimes \tilde{\nabla} \Phi_{0z} = \nabla \mathbf{n} : (A \mathbf{n}) \otimes Q_{z\zeta}. \end{aligned} \quad (3.25)$$

3.4.3 The Default Correction

As mentioned in Remark 14, in the definition $z = (S^N - \varepsilon H_{\varepsilon})/\varepsilon$, the quantity $S^N(x, t) - \varepsilon H(S'(x, t), t)$ is not exactly the distance function from x to the zero level set, Γ_t^{ε} , of $\varphi_{\varepsilon}(\cdot, t)$. This deficiency leads to certain default first order expansion terms. Here we eliminate them by expanding the solution as

$$\Phi(z, s', t) = Q(\mathbf{n}(s', t), z) - \varepsilon Q_{\zeta}(\mathbf{n}(s', t), z) \cdot \nabla H_{\varepsilon}(s', t) + \varepsilon \hat{\Phi}, \quad (3.26)$$

$$\hat{\Phi}(z, s', t) \sim \hat{\Phi}_1(z, s', t) + \varepsilon \hat{\Phi}_2(z, s', t) + \dots. \quad (3.27)$$

Since $Q(\zeta, 0) = 0$, we have $Q_{\zeta}(\zeta, 0) = \mathbf{0}$. Hence, the boundary condition (3.24) is equivalent to

$$\hat{\Phi}_i(\pm\infty, s', t) = 0, \quad \hat{\Phi}_i(0, s', t) = 0 \quad \forall i = 1, 2, \dots.$$

Abbreviating $Q(\mathbf{n}(s', t), z)$ as Q and $Q(\mathbf{n}(s', t), z - y \cdot \mathbf{n}(s', t))$ as \hat{Q} ,

$$\nabla H_{\varepsilon} \cdot \mathcal{L}^{\mathbf{n}} Q_{\zeta} = \nabla H_{\varepsilon} \cdot \left(-2A \mathbf{n} Q_{zz} + (1 - \lambda) \int_{\mathbb{R}^N} J(y) y \hat{Q}_z dy \right). \quad (3.28)$$

Now substituting (3.26), (3.28), and (3.25) into (3.20) and keeping track of the $D^2 H_\varepsilon$ term, we derive that (3.20) is equivalent to

$$-\mathcal{L}^{\mathbf{n}} \hat{\Phi} = \tau v Q_z + u G'(Q) + \nabla \mathbf{n} : B + \varepsilon (\tau Q_z \partial_t H_\varepsilon - D^2 H_\varepsilon : B) + \dots \quad (3.29)$$

where

$$B := \lambda [A Q_z + 2 A \mathbf{n} \otimes Q_{z\zeta}] + (1 - \lambda) \int_{\mathbb{R}^N} J(y) \left\{ \frac{y \otimes y}{2} \hat{Q}_z - y \otimes \hat{Q}_\zeta \right\} dy.$$

3.4.4 The First Order Equation

The first order equation of (3.29) reads

$$-\mathcal{L}^{\mathbf{n}} \hat{\Phi}_1 = \tau v(X_0, t) Q_z + u(X_0, t) G'(Q) + \nabla \mathbf{n}(X_0, t) : B$$

where $X_0 = X_0(s', t)$ is a generic point on Γ_t . The solvability condition (3.15) requires that the following interfacial condition be satisfied on Γ :

$$0 = \tau v(X_0, t) \int_{\mathbb{R}} Q_z^2 dz + u(X_0, t) \int_{\mathbb{R}} G'(Q) Q_z dz + \nabla \mathbf{n}(X_0, t) : \int_{\mathbb{R}} B(z, s', t) Q_z dz.$$

Using Lemma 11 and $\int_{\mathbb{R}} G'(Q) Q_z dz = G(1) - G(-1) = 1$, this condition can be written as

$$u(X_0, t) + \alpha(\mathbf{n}) v(X_0, t) + \nabla \mathbf{n} : D^2 \sigma(\mathbf{n}) = 0$$

where $\mathbf{n} = \mathbf{n}(X_0, t)$, $\alpha(\mathbf{n}) = \tau \int_{\mathbb{R}} Q_z(\mathbf{n}, z)^2 dz$, and $X_0 = X_0(s', t)$ is a generic point on the limit interface Γ_t . This is exactly the equation (1.17). Note that if we use (3.17), then we have

$$\nabla \mathbf{n} : D^2 \sigma(\mathbf{n}) = \sum_{i=1}^{N-1} \kappa^i \tau_i \otimes \tau_i : D^2 \sigma(\mathbf{n}) = \sum_{i=1}^{N-1} \kappa^i \sigma_{\tau_i \tau_i}(\mathbf{n}).$$

Here the direction τ_i in the second order directional derivative $\sigma_{\tau_i \tau_i}$ is assumed to be constant in the differentiation. Consequently, the interfacial condition (1.17) can be written as (1.18).

Assume that this interfacial condition is satisfied. Then there is a unique solution $\hat{\Phi}_1$.

3.4.5 High Order Expansions

The equation for $\hat{\Phi}_{k+1}$, $k \geq 1$, can be written as

$$-\mathcal{L}^{\mathbf{n}} \hat{\Phi}_{k+1} = \tau Q_z \partial_t^\Gamma h_k - \nabla^\Gamma \otimes \nabla^\Gamma h_k : B - C \cdot \nabla^\Gamma h_k - \hat{C} : \nabla^\Gamma h_1 \otimes \nabla^\Gamma h_k - Dh_k - E_k$$

where ∂_t^Γ , ∇^Γ , and $\nabla^\Gamma \otimes \nabla^\Gamma$ are the restrictions of ∂_t , ∇ , and D^2 on Γ respectively; that is,

$$\begin{aligned} \partial_t^\Gamma h(s', t) &:= \sum_{i=1}^{N-1} h_{s^i}(s', t) S_t^i(X_0, t) + h_t(s', t), \\ \nabla^\Gamma h(s', t) &:= \sum_{i=1}^{N-1} h_{s^i}(s', t) \nabla S^i(X_0, t), \\ \nabla^\Gamma \otimes \nabla^\Gamma h(s', t) &:= \sum_{i,j=1}^{N-1} h_{s^i s^j}(s', t) \nabla S^i(X_0, t) \otimes \nabla S^j(X_0, t) + \sum_{i=1}^{N-1} h_{s^i}(s', t) D^2 S^i(X_0, t), \end{aligned}$$

where $X_0 = X_0(s', t)$. Also, C, \hat{C}, D are functions depending only on Q and X_0 , whereas E_k depends only on lower order expansions $\Phi_0, \hat{\Phi}_1, \dots, \hat{\Phi}_k, X_0, h_1, \dots, h_{k-1}$. The solvability condition (3.15) for $\hat{\Phi}_{k+1}$ can be written as

$$\mathcal{L}^\Gamma h_k(s', t) = e_k(s', t) \quad (3.30)$$

where

$$\mathcal{L}^\Gamma := \alpha(\mathbf{n}) \partial_t^\Gamma - D^2 \sigma(\mathbf{n}) : \nabla^\Gamma \otimes \nabla^\Gamma - c(s', t) \cdot \nabla^\Gamma + d(s', t).$$

Here one can verify that $\int_{\mathbb{R}} Q_z \hat{C}(z, s', t) dz = 0$, so there is no $\nabla^\Gamma h_1 \otimes \nabla^\Gamma$ term.

When the matrix $D^2 \sigma(\mathbf{n})$ is positive definite on the tangent space $\{\tau \mid \tau \perp \mathbf{n}\}$, for every $\mathbf{n} \in \mathbb{S}^{N-1}$, (3.30) is a parabolic linear equation defined on the manifold Γ . If we impose appropriate initial and boundary conditions, say, $h_k(s', 0) \equiv 0$ and Γ_t has no boundary, we can solve the parabolic equation to obtain a unique h_k , from which, we obtain a unique $\hat{\Phi}_{k+1}$. The induction can proceed to arbitrary high order expansions.

We summarize our derivation as follows:

Theorem 15. *The solution $\varphi = \varphi_\varepsilon(x, t)$ of (3.3) admits a formal asymptotic expansion only if the interface condition (1.17) is satisfied on the limit interface.*

Remark 16. In general, $h_1 \not\equiv 0$. In [27], for the case of $\lambda = 1$, a special non-linearity of W and G was selected so that the solution of the resulting system of the phase field equations gives $h_1 \equiv 0$. This means that the zero level set of φ_ε is within an $O(\varepsilon^2)$ distance from the limit interface.

3.5 REPRESENTATIONS OF INTERFACIAL CONDITION IN SPECIAL CASES

3.5.1 The Two Dimensional Case

In the two dimensional case, we can express the normal as $\mathbf{n} = (\cos \theta, \sin \theta)$ and the tangent as $\tau = (-\sin \theta, \cos \theta)$. Consequently, using polar coordinates and the homogeneity of σ we can express σ as

$$\sigma(\rho \cos \theta, \rho \sin \theta) = \rho \bar{\sigma}(\theta).$$

Consequently,

$$\begin{aligned} \nabla \sigma(\zeta) &= [\sigma_{\zeta^1} \ \sigma_{\zeta^2}] = [\cos \theta \ \sin \theta] \bar{\sigma}'(\theta) + [-\sin \theta \ \cos \theta] \bar{\sigma}'(\theta), \\ D^2 \sigma(\zeta) &= \begin{bmatrix} \sigma_{\zeta^1 \zeta^1} & \sigma_{\zeta^2 \zeta^1} \\ \sigma_{\zeta^1 \zeta^2} & \sigma_{\zeta^2 \zeta^2} \end{bmatrix} = \begin{bmatrix} -\sin \theta \\ \cos \theta \end{bmatrix} [-\sin \theta \ \cos \theta] \frac{\bar{\sigma}(\theta) + \bar{\sigma}''(\theta)}{\rho}, \\ \tau \otimes \tau : D^2 \sigma(\mathbf{n}) &= \tau^T D^2 \sigma(\mathbf{n}) \tau = \bar{\sigma}(\theta) + \bar{\sigma}''(\theta). \end{aligned}$$

Thus, in the 2-dimensional case, Gibbs-Thomson relation can be written as (1.10).

3.5.2 Interfacial Condition Using Distance Function

Let $h(x, t)$ be the signed distance from x to Γ_t , positive in the liquid region and negative in the solid region. Then $h(x, t) = S^N(x, t)$, $\nabla h(x, t) = \mathbf{n}$, and $D^2 h = \nabla \mathbf{n}$. Also, $v = -h_t$. Hence, the interfacial condition (1.17) can be expressed as

$$\alpha(\nabla h)h_t = u + \sum_{i,j=1}^N \sigma_{\zeta^i \zeta^j}(\nabla h)h_{x^i x^j} \quad \text{on } \Gamma = \{h = 0\}. \quad (3.31)$$

This equation is valid only on Γ . Off the set, the governing equation for h is $|\nabla h| = 1$.

3.5.3 Interfacial Condition Using Level Sets

Suppose the interface Γ is represent by the non-degenerate zero level set of a function Ψ , i.e. $\Gamma_t = \{x \mid \Psi(x, t) = 0\}$ with $\nabla \Psi \cdot \mathbf{n} > 0$ on Γ_t . Then there exists a positive function C such that in a small neighborhood of

$$h(x, t) = C(x, t)\Psi(x, t).$$

Consequently,

$$h_t = C\Psi_t + C_t\Psi, \quad \nabla h = C\nabla \Psi + \Psi\nabla C, \quad D^2h = CD^2\Psi + \nabla C \otimes \nabla \Psi + \nabla \Psi \otimes \nabla C + \Psi D^2C.$$

Thus, on Γ_t ,

$$\begin{aligned} h &= \Psi = 0, \quad \nabla h = C\nabla \Psi, \quad C = \frac{1}{|\nabla \Psi|}, \\ h_t &= C\Psi_t = \frac{\Psi_t}{|\nabla \Psi|}, \quad D^2h = \frac{D^2\Psi}{|\nabla \Psi|} + \nabla C \otimes \nabla \Psi + \nabla \Psi \otimes \nabla C. \end{aligned}$$

Since (3.12) implies that $\nabla \Psi \cdot D^2\sigma(\mathbf{n}) = \mathbf{0}$ and $D^2\sigma(\mathbf{n}) \cdot \nabla^T \Psi = \mathbf{0}$, we then obtain, on Γ ,

$$\begin{aligned} \nabla \mathbf{n} : D^2\sigma(\mathbf{n}) &= D^2h : D^2\sigma(\mathbf{n}) = \frac{D^2\Psi}{|\nabla \Psi|} : D^2\sigma(\mathbf{n}) = D \left(\frac{\nabla \Psi}{|\nabla \Psi|} \right) : D^2\sigma(\mathbf{n}) \\ &= \sum_{i,j=1}^N \sigma_{\zeta^i \zeta^j} \left(\frac{\nabla \Psi}{|\nabla \Psi|} \right) \frac{\partial}{\partial x^i} \left(\frac{\Psi_{x^j}}{|\nabla \Psi|} \right) = \sum_{i=1}^N \frac{\partial}{\partial x_i} \sigma_{\zeta^i} \left(\frac{\nabla \Psi}{|\nabla \Psi|} \right) = \operatorname{div} \left(\sigma_{\zeta} \left(\frac{\nabla \Psi}{|\nabla \Psi|} \right) \right). \end{aligned}$$

Finally, recalling that the normal velocity of the interface is given by $v = -h_t = -\Psi_t/|\nabla \Psi|$, the interfacial condition (1.17) thus can be written as (1.19). Unlike (3.31), equation (1.19) can be regarded as valid in the whole space, whose viscosity solutions have been well-studied; see, for example, Evans-Soner-Souganidis [86] and Chen-Giga-Goto [87].

3.5.4 A Three Dimensional Example

Assume that the anisotropy is given by, for positive constants a, b, c ,

$$\sigma(\zeta) = \frac{a(\zeta^1)^2 + b(\zeta^2)^2 + c(\zeta^3)^2}{|\zeta|} \quad \forall \zeta = (\zeta^1, \zeta^2, \zeta^3)^T \in \mathbb{R}^3 \setminus \{0\}.$$

Then

$$\begin{aligned} \nabla \sigma(\zeta) &= \frac{[2a\zeta^1 \ 2b\zeta^2 \ 2c\zeta^3]}{|\zeta|} - \frac{\zeta^T \sigma}{|\zeta|^2}, \\ D^2 \sigma(\zeta) &= \frac{(2a, 2b, 2c)}{|\zeta|} - \frac{\sigma I}{|\zeta|^2} + \frac{3\sigma}{|\zeta|^2} \zeta \otimes \zeta \\ &\quad - \frac{2}{|\zeta|^3} \{[a\zeta^1 \ b\zeta^2 \ c\zeta^3] \otimes \zeta + \zeta \otimes [a\zeta^1 \ b\zeta^2 \ c\zeta^3]\}. \end{aligned}$$

Now let $h(x, t) = S^N(x, t)$ be the signed distance from x to the interface Γ_t . Then $\mathbf{n} = \nabla h$ and $\nabla \mathbf{n} = D^2 h$. Using $\mathbf{n}^T D^2 h = (0)_{1 \times N}$ and $D^2 h \mathbf{n} = (0)_{N \times 1}$ we obtain

$$\nabla \mathbf{n} : D^2 \sigma(\mathbf{n}) = 2ah_{x^1 x^1} + 2bh_{x^2 x^2} + 2ch_{x^3 x^3} - (ah_{x^1}^2 + bh_{x^2}^2 + ch_{x^3}^2) \Delta h.$$

The operator on the right-hand side is elliptic for every $\mathbf{n} = \nabla h \in \mathbb{S}^{N-1}$ if and only if

$$2 \min\{a, b, c\} > \max\{a, b, c\}$$

3.6 THE WULFF SHAPE—A NUMERICAL EXAMPLE

We consider a special two dimensional case where J is given in polar coordinates by

$$J(x, y) = \bar{J}(r, \theta) = J_0(r) + \delta \cos(n\theta) J_1(r), \quad r = \sqrt{x^2 + y^2}, \quad \tan \theta = \frac{y}{x},$$

where n is an even positive integer. For $\mathbf{n} = (\cos \theta, \sin \theta)$ we write $j(\mathbf{n})$ and $\sigma(\mathbf{n})$ as $\bar{j}(\theta)$ and $\bar{\sigma}(\theta)$ respectively. Then

$$\begin{aligned} \bar{j}(\theta, z) &= \int_{-\infty}^{\infty} J(z \langle \cos \theta, \sin \theta \rangle + \ell \langle -\sin \theta, \cos \theta \rangle) d\ell \\ &= \int_{-\infty}^{\infty} \bar{J} \left(\sqrt{z^2 + \ell^2}, \theta + \arctan \frac{\ell}{z} \right) d\ell \\ &= \hat{j}(\delta \cos n\theta, z) \end{aligned}$$

where

$$\begin{aligned} \hat{j}(h, z) &= j_0(z) + h j_n(z), \\ j_0(z) &= 2 \int_0^{\infty} J_0(\sqrt{z^2 + \ell^2}) d\ell, \\ j_n(z) &= 2 \int_0^{\infty} J_1(\sqrt{z^2 + \ell^2}) \cos \left(n \arctan \frac{\ell}{z} \right) d\ell. \end{aligned}$$

As an illustration, we choose the following:

$$n = 6, \quad J_0(r) = \frac{e^{-r^2}}{\pi}, \quad J_1(r) = -\frac{r^6 e^{3-2r^2}}{27\pi}.$$

Then

$$j_0(z) = \frac{e^{-z^2}}{\sqrt{\pi}}, \quad j_6(z) = \frac{e^{3-2z^2}(15 - 180z^2 + 240z^4 - 64z^6)}{1728\sqrt{2}\pi}.$$

The function $\hat{j}(h, \cdot) := j_0(\cdot) + h j_6(\cdot)$ is shown in Figure 4(a). It is easy to verify that

$$\begin{aligned} J(x, y) \geq 0 \quad \forall (x, y) \in \mathbb{R}^2 &\iff |\delta| \leq 1, \\ \bar{j}(\theta, z) = \hat{j}(\delta \cos n\theta, z) \geq 0 \quad \forall \theta \in [0, 2\pi], z \in \mathbb{R} &\iff |\delta| \leq 6.15285 \dots \end{aligned}$$

For each $h \in [-12, 12]$, we denote by $\hat{Q}(h, \cdot)$ the solution Q of (3.8) with

$$\lambda = 0, \quad j(\zeta, z) = \hat{j}(h, z), \quad W(q) = \frac{(1 - q^2)^2}{4}.$$

Then (3.8) can be written as

$$\hat{j}(h) * \hat{Q}(h) = \hat{Q}^3(h).$$

Numerically, we compute the solution by the iteration scheme

$$Q_0(z) = \tanh(z), \quad Q_{k+1} = \sqrt[3]{\hat{j}(h) * Q_k}, \quad \hat{Q}(h, \cdot) = \lim_{k \rightarrow \infty} Q_k(\cdot).$$

The solution $\hat{Q}(h, \cdot)$ is shown in Figure 4(b). For $h \in [11, 12]$, we find that $\hat{Q}(h, \cdot)$ is not monotonic; this is caused in part by the fact that $\hat{j}(h, \cdot)$ is not positive when $h \geq 6.15 \dots$. The corresponding surface energy density, plotted in Figure 4(c), is calculated by

$$\hat{\sigma}(h) = \int_{\mathbb{R}} \left(W(Q) - \frac{1}{2} Q W'(Q) \right) dz = \frac{1}{4} \int_{\mathbb{R}} \left(1 - \hat{Q}^4(h, z) \right) dz.$$

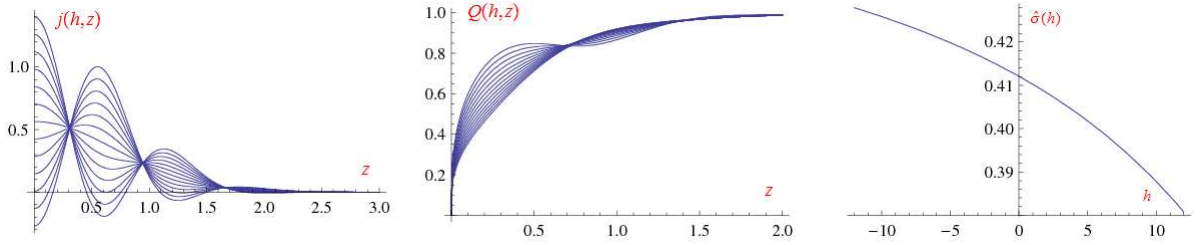


Figure 4: The functions $\hat{j}(h, z); \hat{Q}(h, z); \hat{\sigma}(h)$

Now for fixed δ , denoting $\mathbf{n} = (\cos \theta, \sin \theta)$ we have

$$Q(\mathbf{n}, z) = \hat{Q}(\delta \cos(6\theta), z), \quad \sigma(\mathbf{n}) = \bar{\sigma}(\theta) = \hat{\sigma}(\delta \cos(6\theta)).$$

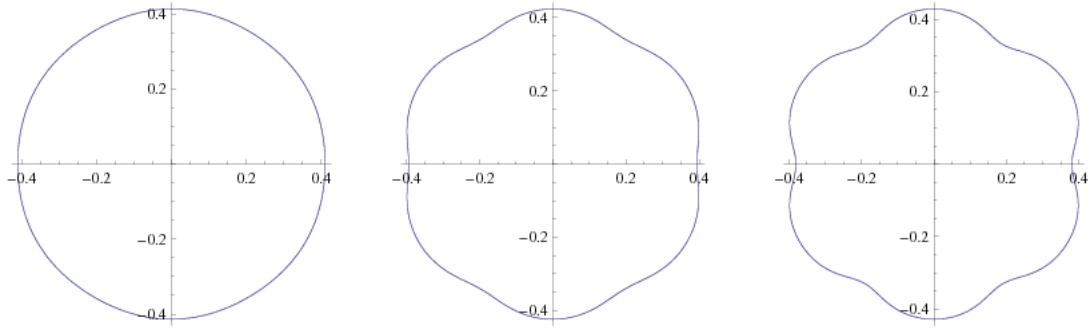
From the plot of $\hat{\sigma}(\cdot)$ in Figure 4(c), we see that

$$\hat{\sigma}(h) \approx 0.412062 - 0.00177 h - 0.0000500 h^2.$$

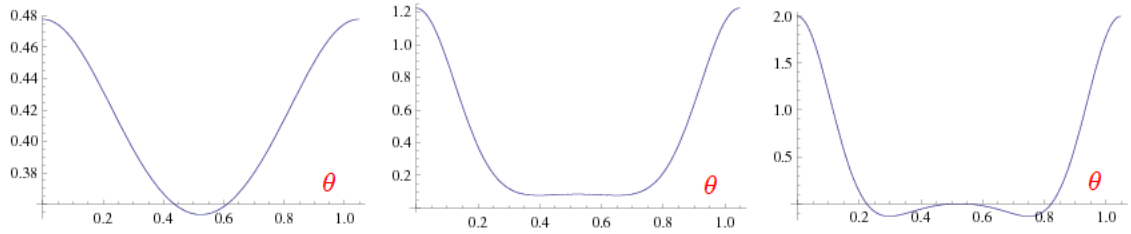
Thus,

$$\begin{aligned} \bar{\sigma}(\theta) &\approx 0.412062 - 0.00177 \delta \cos(6\theta) - 0.0000500 \delta^2 \cos^2(6\theta), \\ \bar{\sigma}'(\theta) &\approx \delta[0.0106 + 0.000600 \delta \cos(6\theta)] \sin(6\theta), \\ \bar{\sigma}''(\theta) &\approx \delta[0.0639 \cos(6\theta) + 0.00360 \delta \cos(12\theta)]. \end{aligned}$$

Counterplot of $\bar{\sigma}(\theta)$



$\bar{\sigma}(\theta) + \bar{\sigma}''(\theta)$



Wulff Shape

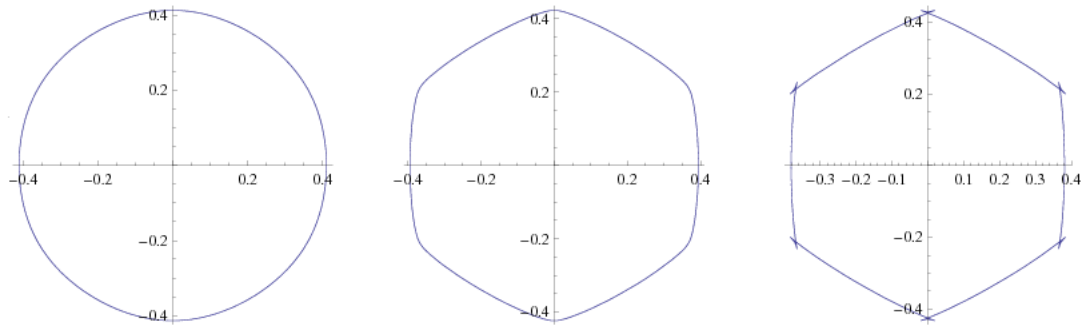


Figure 5: The functions $\bar{\sigma}(\theta)$; $\bar{\sigma}(\theta) + \bar{\sigma}''(\theta)$; The Wulff Shapes

For $\delta = 1, 8$ and 12 , the functions $\bar{\sigma}(\theta) = \hat{\sigma}(\delta \cos(6\theta))$ and $\bar{\sigma}(\theta) + \bar{\sigma}''(\theta)$ are plotted in Figure 5. Numerically, we find that $\bar{\sigma}(\theta) + \bar{\sigma}''(\theta) > 0$ for all $\theta \in [0, 2\pi]$ when $|\delta| < 9.78 \dots$.

The **Wulff shape** is the shape of a solid under the undercooling temperature $u \equiv -1$. From (1.10), the Wulff shape can be computed in terms the surface energy density as follows. Denote the boundary of the Wulff shape by $x = X(\theta)$ where $\theta \in [0, 2\pi]$ and $\langle \cos \theta, \sin \theta \rangle$ is the unit normal at $X(\theta)$. Then, with respect to the arclength parameter s , we have

$$\frac{dX}{d\theta} = \frac{dX}{ds} \frac{ds}{d\theta} = \langle -\sin \theta, \cos \theta \rangle \frac{ds}{d\theta}, \quad \frac{d\theta}{ds} = \kappa = \frac{1}{\bar{\sigma}(\theta) + \bar{\sigma}''(\theta)}.$$

It then follows that

$$\frac{dX(\theta)}{d\theta} = [\bar{\sigma}(\theta) + \bar{\sigma}''(\theta)] \langle -\sin \theta, \cos \theta \rangle.$$

After integration, we obtain the function for the boundary of the Wulff shape:

$$X(\theta) = \bar{\sigma}(\theta) \langle \cos \theta, \sin \theta \rangle + \bar{\sigma}'(\theta) \langle -\sin \theta, \cos \theta \rangle, \quad \theta \in [0, 2\pi].$$

For $\delta = 1, 8, 12$, the Wulff shapes are given in the third row in Figure 5. When $\delta \in [9.79, 12]$, the function $\bar{\sigma} + \bar{\sigma}''$ is not positive; the corresponding Wulff shape is close to a hexagon with “ears” at the vertices.

4.0 A REALISTIC APPLICATION: LENNARD-JONES SYSTEMS

As noted in the introduction chapter, for the surface tension, a common conclusion of all experimental and computational studies is that regardless of the inter-atomic potential, its value in the $[110]$ direction is slightly less than the surface tension in the $[100]$ direction. Furthermore, simulations and some theoretical calculations indicate that surface tensions of Lennard-Jones systems at the triple temperature is approximately $\gamma = 0.37\varepsilon/\sigma^2$ where ε, σ are material constants.

Although the explicit approach above that we introduced in the previous chapter takes the microscopic effects into account, it is not immediately clear how one can use a continuum method to model a system whose particles sit on a discrete lattice. This is a serious issue, since, the same type of interactions can lead to different surface tension values and anisotropies in different lattice structures. (Generally the surface tension anisotropy is lower in systems whose solid phase has a *bcc* structure lattice than for those with *fcc* structure).

Due to the points noted above, in this paper, we pursue a more convenient strategy that eliminates this difficulty. Instead of using a continuum free energy involving derivatives of phase field as an approximation to the interaction energy, we shall use the full discrete Hamiltonian on the actual lattice and derive a discrete equation for equilibrium. We then solve the resultant equation for the particular case of a planar interface. Once the particular solution is obtained, it will be used to calculate the surface tension whose definition is modified to fit the discrete structure.

A method that has recently been popular to study the interfacial properties is the phase field crystal (PFC) method, a diffuse interface model that takes the crystal structure into account. The main difference between PFC method and our method is that our potential is non local where in PFC the free energy consists of local term only.

4.1 THE DISCRETE PHASE FIELD MODEL

We consider an excess free energy functional of the form.

$$F[\phi] = \frac{1}{4} \sum_{x,y \in \Omega} J(x-y)(\phi(x) - \phi(y))^2 + \sum_{x \in \Omega} W(\phi(x)) \quad (4.1)$$

Here x, y are points on the lattice, J is the interaction potential, W is the double well potential and ϕ is the phase function that takes the constant value 0 in the solid and 1 in the liquid bulk. The form of the interaction term reflects that it is actually an excess free energy where the infinite contribution of bulks sides are subtracted out.

It is customary to replace singular entropic potential by a smooth function for theoretical and computational purposes. In doing so we do not want to suppress its physical effect. So, we are going to choose a reasonable well depth, (i.e. "a").

$$\begin{aligned} W(\phi) &= kT(-\phi \ln \phi - (1 - \phi) \ln(1 - \phi)) \\ &\simeq kT(\phi - \phi^2)^2/a \end{aligned}$$

Next, we look for the extremum of F . Then, by variational argument, we obtain the following:

$$- \| J \| \phi(x) + J * \phi(x) = W'(\phi(x)) \quad (4.2)$$

where

$$\begin{aligned} J * \phi(x) &:= \sum_y \phi(x-y)J(y) \\ \| J \| &:= \sum_{\substack{x \in \Omega \\ x \neq 0}} J(x) \end{aligned}$$

Let $x_0 \in \mathbb{Z}^3$ be a point on the lattice and let $\{x \mid \phi(x_0, t) = 1/2\}$ denote the interface as a level set. We seek solutions of equation (4.2) of the form

$$\phi(x, t) = P(\zeta, \sqrt{2}(x - x_0) \cdot \zeta) = P(\zeta, z)$$

where x is an arbitrary lattice point in the crystal.

Let $e_1 = \frac{1}{\sqrt{2}} < 1, 1, 0 >$, $e_2 = \frac{1}{\sqrt{2}} < 1, 0, 1 >$, $e_3 = \frac{1}{\sqrt{2}} < 0, 1, 1 >$ be the base vectors of the lattice and ζ be a vector (with integer valued components such as $< 1, 1, 1 >$) that is normal to the level set of ϕ . Then, the equation (4.2) takes the form

$$0 = - \| J \| P(\zeta, z) + \sum_{y \in \Omega} P(\zeta, z - \sqrt{2}y \cdot n) J(y) - W'(P(z)) \quad (4.3)$$

$$\lim_{z \rightarrow -\infty} P(\zeta, z) = 0, \quad \lim_{z \rightarrow +\infty} P(\zeta, z) = 1, \quad P(0) = 1/2$$

Our task is then to solve the above "sum equation" (analogous to the integral equation in the continuum case). In order to solve this equation for $P(j)$ ($j \in \mathbb{Z}$) we will use the analog of the auxiliary time iteration (Lemma 9) technique of the previous chapter. However, we note that the theorem above is proved for the continuum problem. Nevertheless, it suggests a numerical scheme for the discrete problem that will be used to calculate the eventual phase profile.

4.2 RESULTS AND DISCUSSIONS

4.2.1 Numerical Solutions

Let us assume that particles interact through Lennard-Jones potential, i.e.,

$$J(x) := \begin{cases} 4\varepsilon \left(-\frac{\sigma^{12}}{|x|^{12}} + \frac{\sigma^6}{|x|^6} \right) & \text{if } |x| \leq 5d \\ 0 & \text{if } |x| > 5d \end{cases}$$

For simplicity one can take $x_0 = 0$. The interface thickness is roughly several atomic distances long. We generate a portion of the lattice (denoted by Ω) using independent base vectors by $i \cdot e_1 + j \cdot e_2 + k \cdot e_3$ where $i = -i_{\max} \dots i_{\max}$, $j = -j_{\max} \dots j_{\max}$, $k = -k_{\max} \dots k_{\max}$. Since the interaction decays with the sixth power of the inverse of the distance, the range of i, j, k need not be very large. By an easy computation we see that, for $i_{\max} = j_{\max} = k_{\max} = 6$,

$\| J \| = 4.279$. This value does not change appreciably for greater values of i, j, k . Hence we choose $i_{\max} = j_{\max} = k_{\max} = 10$.

In our calculations we scaled the system so that the physical quantities can be written in terms of the basic parameters of the problem. (e.g. surface tension can be expressed in terms of ε/d^2 where " $d = 1.09\sigma$ " is the nearest neighbor distance).

We want to solve equation (4.3) numerically. Using the idea of the lemma, one expects that, for small values of Δt and reasonable initial profile (e.g. hyperbolic functions), the following iterative process converges

$$\begin{aligned}
f_{k+1}(z) &= f_k(z) + \Delta t \left\{ - \| J \| f_k(z) + \sum_y f_k(z - \sqrt{2}y \cdot n) J(y) \right. \\
&\quad \left. - \frac{kT}{\varepsilon} (f_k(z) - f_k^2(z))(f_k(z) - 1/2)/a \right\} \\
f_0(z) &= (1 + \tanh(z))/2
\end{aligned} \tag{4.4}$$

As noted earlier, for the double well potential, we use a smooth function instead of a singular one and estimate the value for a so that both functions $W_1(x) = -x \ln x - (1-x) \ln x$ and $W_2(x) = (x - x^2)^2/a$ will be close to each other in some sense. A reasonable choice is that " a " be the value for which the functions will be close each other in their average values. In this case $a \simeq 1/15$. Another choice can be that the maximum values of the both functions (which are at $x = 1/2$) will be close to each other. This approximately gives $a \simeq 1/11$. In most phase field models " a " is taken as a phenomenological parameter which is related to interface thickness in a certain way. Depending on this relation different macroscopic sharp interface models can be obtained as limiting cases of phase field equations.

We choose $\Delta t = 0.01$, $a = 1/15$ and $i_{\max} = j_{\max} = k_{\max} = 10$. Using the scheme above we truncate the iteration when the maximum of difference between two successive f_k is less than $\delta = 0.0003$. The obtained solution profiles at the triple point $T^* = kT/\varepsilon = 0.70$ in an fcc lattice are given above in figure-6.

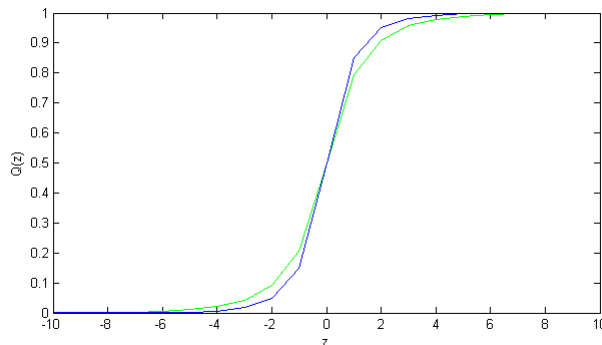


Figure 6: The discrete phase profile

Based on the solution profile one can roughly estimate the interface thickness. If we view the points of the lattice where $Q(\cdot, z) < 0.1$ as "essentially liquid" and $Q(\cdot, z) > 0.9$ "essentially solid" then the interface thickness is found to be approximately " $3d$ " long.

4.2.2 Surface Tension

In this subsection, we modify the definition of the surface tension in a way that will make the notion meaningful for discrete systems. We shall derive an expression for the surface tension and in the next subsection we will compute this quantity using a slightly different form of the interaction potential in order to compare our results with the ones in the literature.

Surface tension is understood through a local interpretation of the free energy. Generally, it is defined as the excess free energy per unit area. So, given a direction ζ in the discrete lattice, we need to choose a region in which we can calculate the free energy per unit area. Let us write the total free energy in a more suitable form

$$\begin{aligned}
F[\phi] &= \frac{1}{2} \| J \| \sum_{x \in \Omega} \phi(x)^2 - \frac{1}{2} \sum_{x, y \in \Omega} J(x-y) \phi(x) \phi(y) + \sum_{x \in \Omega} W(\phi(x)) \\
&= \frac{1}{2} \| J \| \sum_{w\hat{t} \perp \hat{\zeta}} \sum_z P(\zeta, z)^2 \\
&\quad - \sum_{w\hat{t} \perp \hat{\zeta}} \frac{P(\zeta, z)}{2} \sum_z \left(\sum_{y \in \Omega} P(\zeta, z - \sqrt{2}y \cdot n) J(y) \right) + \sum_{w\hat{t} \perp \hat{\zeta}} \sum_z W(P(\zeta, z))
\end{aligned} \tag{4.5}$$

where, in the second equality above, the summations are taken over all z ($z \in \mathbb{Z}$) and w ($w\hat{t} \perp \hat{\zeta}$) such that $z\hat{\zeta} + w\hat{t} \in \Omega$. Notice that, for fixed z , the phase function $P(\zeta, z)$ has constant values on all points x for which $\sqrt{2}x \cdot \zeta = z$. Then it makes sense to talk about the plane that contains all such points. Consider now a rectangular region on that plane in the direction ζ (see figure 7). We can imagine a tube that goes through the interfacial region that is formed by moving the rectangle along the $-\vec{\zeta}, \vec{\zeta}$ direction. We calculate the contributions of all the points within that tube to the free energy and divide the result by the cross sectional area of the same tube. Obviously, the number of the lattice points and the cross sectional area will change with the geometry of the lattice. Using equation (4.3) and ignoring the contribution to the free energy near the bulk sides (which is nearly zero for $|z| > i_{\max}$) one can write the following expression for the surface tension

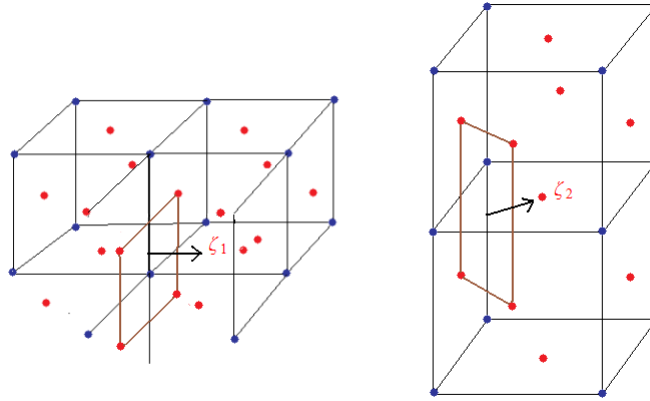


Figure 7: Cross sectional areaa for (100) and (110) planes

$$\gamma(\zeta) = \frac{\sum_{\substack{x \cdot \zeta = z = -i_{\max} \dots i_{\max} \\ x \text{ intersects the tube}}} W(P(\zeta, z)) - W'(P(\zeta, z))P(\zeta, z)/2}{\text{Cross area of the tube}}.$$

As an illustration, for the potential defined in [49], we find the surface tension for $\zeta_1 = [100]$ at the triple point as follows:

Define $f(\zeta, z) := W(P(\zeta, z)) - W'(P(\zeta, z))P(\zeta, z)/2$. Let the points x satisfying $x \cdot \zeta_1 = z = 0$ denote the interface plane. Then, we observe that (figure 7-a), for $z = \text{even}$, the site in the center of the brown square lies completely inside the tube and the four other sites on the corners are shared by four squares (including the brown square). On the other hand, for $z = \text{odd}$, each of the four sites touching the tube is sitting on one side of the brown square and each of them is shared by two squares. Hence the surface tension can be written as

$$\begin{aligned} \gamma(\zeta_1) &= \frac{\sum_{\substack{z = -i_{\max} \dots i_{\max} \\ z \text{ even}}} f(\zeta_1, z) + 4f(\zeta_1, z)/4 + \sum_{\substack{z = -i_{\max} \dots i_{\max} \\ z \text{ odd}}} 4f(\zeta_1, z)/2}{(d\sqrt{2})^2} \\ &= \frac{\sum_{z = -i_{\max} \dots i_{\max}} f(\zeta_1, z)}{d^2} \end{aligned} \quad (4.6)$$

A similar argument can be used for the surface tension in $\zeta_2 = [110]$ direction. We see from figure 7-b that, for $z = \text{even}$, the site in the center of brown rectangle is completely inside the tube. However, for $z = \text{odd}$, there are four sites sitting at the corners of the brown rectangle each of which is shared by four rectangles. Hence, the surface tension in the ζ_2 direction is given by

$$\begin{aligned} \gamma(\zeta_2) &= \frac{\sum_{\substack{z = -i_{\max} \dots i_{\max} \\ z \text{ even}}} f(\zeta_2, z) + \sum_{\substack{z = -i_{\max} \dots i_{\max} \\ z \text{ odd}}} 4f(\zeta_2, z)/4}{d(d\sqrt{2})} \\ &= \frac{\sum_{z = -i_{\max} \dots i_{\max}} f(\zeta_2, z)}{\sqrt{2}d^2} \end{aligned} \quad (4.7)$$

Using the numerical solutions for $P(\zeta_1, z)$ and $P(\zeta_2, z)$, one finds the surface tension values as

$$\gamma(\zeta_1) = 1.738 \, \varepsilon/d^2 \quad (4.8)$$

$$\gamma(\zeta_2) = 1.695 \, \varepsilon/d^2$$

4.2.3 Anisotropy of the Solid-Liquid Interface

The calculated values above are the surface tension for the solid-gas interface. However, one can find the value of the solid-liquid interface using the argument that the surface tension must be proportional to the latent heat (the "broken bond" argument), i.e.,

$$\gamma_{solid-liquid} \sim L_{solid-liquid} \quad (4.9)$$

$$\gamma_{liquid-gas} \sim L_{liquid-gas}$$

Then we have $\gamma_{solid-gas} = \gamma_{solid-liquid} + \gamma_{liquid-gas}$. Also, assuming that $\gamma_{liquid-gas}$ is isotropic, we can write

$$\gamma_{liquid-gas} = \gamma_{solid-gas}^{avg} \frac{L_{liquid-gas}}{L_{solid-liquid} + L_{liquid-gas}} \quad (4.10)$$

where $\gamma_{solid-gas}^{avg} = \frac{\gamma(\zeta_1) + \gamma(\zeta_2)}{2}$. The ratio $L_{liquid-gas} / (L_{solid-liquid} + L_{liquid-gas})$, for Lennard-Jones systems, is characteristic (with the exception of *He* where the quantum effects become more dominant) and approximately equal to 0.847. For instance, for the 8A Group elements Argon, Krypton and Xenon, this ratio is 0.845, 0.847, 0.848 respectively. Hence, we find $\gamma_{liquid-gas} = 1.716 \varepsilon / d^2$. Then, the solid-liquid surface tension values are found as

$$\gamma_{100} = 0.284 \varepsilon / d^2 = 0.217 \varepsilon / \sigma^2 \quad (4.11)$$

$$\gamma_{110} = 0.241 \varepsilon / d^2 = 0.184 \varepsilon / \sigma^2$$

The anisotropy is traditionally defined to be the relative ratio of the surface tension values, i.e.,

$$\delta = \frac{\gamma_{100} - \gamma_{110}}{\gamma_{solid-liquid}^{avg}}$$

Comparing our results with values in the literature, we see that the values obtained in recent simulations (see Ruslan & Davidchack (RD) [49] and Morris & Song (MS) [53]) with a modified Lennard-Jones potential at the temperature $T^* = 0.62$ are relatively higher than our results (see Table-1).

Earlier simulations of Broughton and Gilmer (BG) [46] predicted value of the surface tension also in the same order of magnitude but the sign of the anisotropy was negative. It

Table 1: Surface Tension Values

Table 1	Our work	MS	RD	BG
γ_{100}	0.217	0.369	0.371	0.34
γ_{110}	0.184	0.361	0.360	0.36
$\frac{\Delta\gamma}{\gamma_{avg}}$	16%	2.2%	3%	5.7%

became an issue for some time to estimate the correct sign. The recent simulations support the reverse order. Our calculation at the triple point also predicts the same ordering with the recent simulations [49], [53], i.e., $\gamma_{100} > \gamma_{110}$. A list of the old and new results is shown in Table-1.

From the table, it is seen that, the absolute value of the surface tension values are about half of the values obtained by the simulations. This discrepancy could be attributed to imprecise estimation of the depth of the double well potential W . As mentioned earlier, one may choose to treat "a" as variable and match the results with values of other works. Nevertheless, the fact that even such a crude estimate can produce reasonably close values is an indication of the model's ability to capture the essential physics.

5.0 CONCLUSION

In this thesis, we pursued the problem of anisotropy from two different perspectives using a diffuse interface approach. Our concern was to develop a semi-microscopic method that would do both confirm the existing sharp interface results and enable us to calculate the physically important properties of real systems.

The first chapter was intended to be a historical review of the developments in the field bringing the story to this date. The concepts and references that were cited are the ones which we found to be more relevant to the theme of this thesis.

In the second chapter, we followed the path of [20], [21] deriving higher order approximations to the free energy in order to improve the existing models. By this way, we were able to obtain the celebrated Herring's condition in the sharp interface limit. The technique also gave some insight on why one needed the extra terms in the free energy for the inclusion of anisotropy into the model. Hence we believe that the generalized formulation considerably resolves the skepticism against a single order parameter models "to be a realistic description of underlying physics".

However, there are still analytical issues that need to be solved with this approach. The mathematical problem involves proving the existence and uniqueness of the phase field equation which may be challenging. Even for the stationary problem, i.e., the corresponding ordinary differential equation, it is not a easy task to handle. Another remaining issue in the same problem is the analysis of numerical solutions. Especially for the ordinary differential equation, the author is investigating the usability of interpolation methods in this regard.

The third chapter handled the problem of anisotropy in a more direct way also aiming at getting a semi-microscopic description. In the past, there have been attempts with a similar intention using a probabilistic approach [71], [75], [72], [73], [74]. The main difference between

our work and the theirs is that we focussed on obtaining macroscopic interfacial condition starting from a mesoscopic model rather than considering purely microscopic dynamics with their probabilistic limits.

There are a number of nice things that come for free with approach of Chapter 3. First and foremost, it is a physically exact model in the sense that no approximation are introduced for the interaction Hamiltonian. Secondly, the existence and uniqueness of solutions were already proven [80]. Thirdly, the results are valid in arbitrary dimensions. Therefore dynamic extensions of this method can be used to model crystal growth and grain boundary motion and the results can be compared with those obtained by other methods [68]. The method also helps to see the connection between the Hoffman-Cahn capillarity vector formulation of interfaces within the context of phase field models, that is, the gradient of the interfacial free energy density function yields the ξ - *vector*.

Chapter 4 was concerned with putting these ideas into practice by calculating the certain physical quantities for a Lennard-Jones system. The virtue of the technique was its suitability to the discrete lattice structure which is the origin of anisotropy. Our aim in this chapter was to get realistic results that can be tested by computer simulations or experiments. We used a modified discrete phase field equation and solved it to find the interfacial free energy of the solid-vapour interface. We were able to calculate the γ in [100] and [110] directions. However calculating γ for [111] requires more care and is not immediately obvious. Nevertheless, the two directions is enough to make an estimate of the anisotropy. It was found that the surface tension in the [100] direction was greater in value than the surface tension in the [110] direction which is in agreement with recent simulations. However, the absolute values obtained were somewhat lower than the ones in the literature.

In the literature there exist other diffuse interface models which take the discrete structure of the solid into account such as phase field crystal models (PFC). The main difference between our model and PFC is that our interaction potential is non-local where as in PFC the free energy consists of local terms only. Another nice feature of our method is its flexibility. For different kinds of materials one can essentially repeat the same procedure just by changing the interaction potential.

A future goal that the author is willing to undertake is to apply the formalism to a broader

set of physical phenomena. To do that, one needs to understand the physical ingredients of the new phenomena that is under study and cast it to the framework of phase field model. One such problem involves the interface properties of alloys. Using the techniques that was developed in this thesis, one can determine the interfacial conditions and interfacial free energy of alloys.

6.0 APPENDIX

Here, we derive, for an arbitrary dimension, the interfacial condition of isotropic systems with with the approach of Chapter 2.

We begin our task by parametrizing the n dimensional sphere:

$$\begin{aligned}
 x_1 &= r \cos \theta_1 \\
 x_2 &= r \sin \theta_1 \cos \theta_2 \\
 x_3 &= r \sin \theta_1 \sin \theta_2 \cos \theta_3 \\
 &\dots \\
 x_{n-1} &= r \sin \theta_1 \sin \theta_2 \dots \sin \theta_{n-2} \cos \theta_{n-1} \\
 x_n &= r \sin \theta_1 \sin \theta_2 \dots \sin \theta_{n-1} \cos \theta_n.
 \end{aligned} \tag{A.5}$$

This parametrization has the volume element

$$|d\vec{r}| = r^{n-1} \sin^{n-2} \theta_1 \sin^{n-3} \theta_2 \dots \sin \theta_{n-2} dr d\theta_1 \dots d\theta_{n-1} = r^{n-1} dr \prod_{i=1}^{n-2} \sin^{n-i-1} \theta_i d\theta_i. \tag{A.6}$$

Define (with r integrated over $(0, R_\infty)$, θ_1 over $(0, 2\pi)$, $\theta_2, \dots, \theta_n$ over $(0, \pi)$)

$$\begin{aligned}
 A(m, 2k_1, \dots, 2k_n) &= \frac{1}{(2k_1)! (2k_2)! \dots (2k_n)!} \int \dots \int (r \cos \theta_1)^{2k_1} (r \sin \theta_1 \cos \theta_2)^{2k_2} \\
 &\quad \cdot \dots (r \sin \theta_1 \sin \theta_{n-2} \cos \theta_{n-1})^{2k_{n-1}} \\
 &\quad \cdot (r \sin \theta_1 \dots \sin \theta_{n-1})^{2k_n} \left\{ dr \prod_{i=1}^{n-2} \sin^{n-i-1} \theta_i d\theta_i \right\}.
 \end{aligned} \tag{A.7}$$

In n -dimensional space, the Hamiltonian will have sums such as

$$\mathcal{R}_m = \sum_{2k_1+2k_2+\dots+2k_n=2m} A(m, 2k_1, \dots, 2k_n) (D_{11}^{k_1} D_{22}^{k_2} \dots D_{nn}^{k_n} \phi). \quad (\text{A.8})$$

Now, we rearrange equation (A.7). We first split the sums as:

$$\sum_{2k_{1,n}=2n} \dots = \sum_{2k_1+2k_{2,n}=2n} \dots \sum_{2k_2+2k_{3,n}=2k_{2,n}} \dots \sum_{2k_{n-2}+2k_{n-1,n}=2k_{n-2,n}} \dots. \quad (\text{A.9})$$

After this splitting, starting from the last sum, we will handle the coupled angular integrals and the summations one by one, yielding

$$\begin{aligned} \sum_{2k_{1,n}=2n} \dots &= \sum_{2k_1+2k_{2,n}=2n} \dots \sum_{2k_2+2k_{3,n}=2k_{2,n}} \dots \\ \sum_{2k_{n-1}+2k_n=2k_{n-1,n}} \int_0^\pi \frac{(\cos^{2k_{n-1}} \theta_{n-1})(\sin^{2k_n} \theta_{n-1})}{(2k_{n-1})!(2k_n)!} d\theta_{n-1} a_n^{k_n} a_{n-1}^{k_{n-1}} \end{aligned} \quad (\text{A.10})$$

where the last term is sorted by comparison with equations (A.7) and (A.8). The calculation of the integral follows exactly the same way as in 2d (Proposition 1 of Section 3). Define:

$$\begin{aligned} f_{n-1} &= \sum_{2k_{n-1}+2k_n=2k_{n-1,n}} \int_0^\pi \frac{(\cos^{2k_{n-1}} \theta_{n-1})(\sin^{2k_n} \theta_{n-1})}{(2k_{n-1})!(2k_n)!} d\theta_{n-1} a_n^{k_n} a_{n-1}^{k_{n-1}} \\ &= \frac{\pi}{(2k_{n-1,n})!!} \sum_{2k_{n-1}+k_n=2k_{n-1,n}} \frac{a_n^{k_n} a_{n-1}^{k_{n-1}}}{k_{n-1}! k_n!} \\ &= 2^{-2k_{n-1,n}} \frac{\pi}{(k_{n-1,n})!(2k_{n-1,n})!!} (a_{n-1,n})^{k_{n-1,n}}. \end{aligned} \quad (\text{A.11})$$

Similarly we define f_{n-2}

$$f_{n-2} = \sum_{2k_{n-2}+k_{n-1,n}=2k_{n-2,n}} \int_0^\pi \frac{(a_{n-2})^{k_{n-2}}}{(2k_{n-2})!} (\cos^{2k_{n-2}} \theta_{n-2})(\sin^{2k_{n-1,n}+1} \theta_{n-2}) f_{n-1}. \quad (\text{A.12})$$

We put f_{n-1} in the above expression for f_{n-2} so that

$$\begin{aligned}
f_{n-2} = & \sum_{2k_{n-1}+k_n=2k_{n-1,n}} \int_0^\pi d\theta \frac{1}{(2k_{n-2})!} (\cos^{2k_{n-2}} \theta_{n-2}) (\sin^{2k_{n-1,n}+1} \theta_{n-2}) \\
& \cdot \left[2^{-k_{n-1,n}} \frac{1}{(2k_{n-1,n})!!} \frac{1}{(k_{n-1,n})!} a_{n-2}^{k_n} (a_{n-1,n})^{k_{n-1,n}} \right]. \tag{A.13}
\end{aligned}$$

Using Proposition 2 (Section 3) we have

$$\begin{aligned}
f_{n-2} &= 2^{-k_{n-2,n}} \frac{1}{(2k_{n-2,n} + 1)!!} \sum_{2k_{n-1}+k_n=2k_{n-2,n}} \frac{a_{n-2}^{k_{n-2}}}{k_{n-2}!} \frac{(a_{n-1,n})^{k_{n-1,n}}}{k_{n-1,n}!} \\
&= 2^{-k_{n-2,n}} \frac{\pi^2}{(2k_{n-2,n} + 1)!!} \frac{1}{k_{n-2,n}!} (a_{n-2,n})^{k_{n-2,n}}.
\end{aligned}$$

Proposition 17. *The f_{n-j} term is given by*

$$f_{n-j} = 2^{-k_{n-j,n}} \frac{\pi^j}{(2k_{n-j,n} + j - 1)!!} \frac{1}{k_{n-j,n}!} (a_{n-j,n})^{k_{n-j,n}} \tag{A.14}$$

where n denotes the dimension.

Proof. We use induction on j and note that the $j = 1$ and $j = 2$ cases have already been established above. Since the “ f ” terms are defined recursively we have

$$\begin{aligned}
f_{n-j} = & \sum_{2k_{n-j}+k_{n-j+1}=2k_{n-j,n}} \int \frac{(a_{n-j})^{k_{n-j}}}{(2k_{n-j})!} (\cos^{2k_{n-j}} \theta_{n-j}) \\
& \cdot (\sin^{2k_{n-j+1,n}+j-1} \theta_{n-j}) f_{n-j+1} (k_{n-j+1,n}) d\theta_{n-j}. \tag{A.15}
\end{aligned}$$

Suppose by the induction hypothesis, the statement is true for the f_{n-j+1} term. We use it in the definition of f_{n-j} to obtain

$$\begin{aligned}
f_{n-j} = & \sum_{2k_{n-j}+k_{n-j+1}=2k_{n-j,n}} \int_0^\pi \frac{(a_{n-j})^{k_{n-j}}}{(2k_{n-j})!} (\cos^{2k_{n-j}} \theta_{n-j}) (\sin^{2k_{n-j,n}+j-1} \theta_{n-j}) \\
& \cdot \frac{\pi^{j-1}}{(2k_{n-j+1,n} + j - 2)!!} \frac{2^{-k_{n-j+1,n}}}{(k_{n-j+1,n})!} (a_{n-j+1,n})^{k_{n-j+1,n}} d\theta_{n-j}. \tag{A.16}
\end{aligned}$$

Once again using the identities for the angular integration, we have

$$f_{n-j} = \sum_{2k_{n-j}+k_{n-j+1}=2k_{n-j,n}} \frac{\pi(a_{n-j})^{k_{n-j}}}{(2k_{n-j})!} \frac{(2k_{n-j+1,n}+j-2)!!}{(2k_{n-j,n}+j-1)!!} \cdot \frac{\pi^{j-1}(2k_{n-j}-1)!!}{(2k_{n-j+1,n}+j-2)!!} \frac{2^{-k_{n-j+1,n}}}{(k_{n-j+1,n})!} (a_{n-j+1,n})^{k_{n-j+1,n}}. \quad (\text{A.17})$$

After considerable calculations, we are left with a simple binomial expansion

$$f_{n-j} = 2^{-k_{n-j,n}} \frac{\pi^j}{(2k_{n-j,n}+j-1)!!(k_{n-j,n})!} \cdot \sum_{2k_{n-j}+k_{n-j+1}=2k_{n-j,n}} \frac{(k_{n-j,n})!}{1} \frac{(a_{n-j})^{k_{n-j}}}{(k_{n-j})!} \frac{(a_{n-j+1,n})^{k_{n-j+1,n}}}{(k_{n-j+1,n})!}.$$

Taking the sum we arrive at our conclusion, (A.14), and the proof is complete. \square

In n dimensions, the Hamiltonian has $n-1$ summations of the type shown above. The only difference will be that the last integration will have limits 0 to 2π . Therefore there will be an extra factor of 2. Apart from that, the last sum can be easily evaluated using the Proposition. The result will yield \mathcal{R}_m . Since $k_{1,n} = m$ and $a_{1,n} = \sum D_{ii} = \Delta$, we have

$$\begin{aligned} \mathcal{R}_m = f_{n-1} &= 2^{-k_{1,n}} \frac{2\pi^{n-1}(a_{1,n})^{k_{1,n}}}{(2k_{1,n}+n-2)!!(k_{1,n})!} \\ &= \frac{1}{2^{m-1}} \frac{\pi^{n-1}}{(2m+n-2)!!m!} (\Delta)^m. \end{aligned} \quad (\text{A.18})$$

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